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Señor
DIRECTOR DIVISIÓN DE NUEVAS CREACIONES
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
E. S. D.

REF: Expediente No. 07 053788- solicitud de patente de invención a favor de **SEOUL NATIONAL UNIVERSITY INDUSTRY FOUNDATION**. Título **PROCESO NOVEDOSO PARA LA PRODUCCION A GRAN ESCALA DE NANOPARTICULAS MONODISPERSAS**.

RESPUESTA A EXAMEN DE FONDO

JUAN PABLO CADENA SARMIENTO, portador de la tarjeta profesional No. 57.492 del C.S.J., obrando como apoderado de la sociedad solicitante me permito dar respuesta al oficio número 17673 relacionado con la patentabilidad de la presente invención y notificado por fijación en lista el 11 de noviembre de 2011.

1. Claridad

En primer lugar, respetuosamente manifestamos nuestro completo desacuerdo con las objeciones por claridad a las reivindicaciones de la presente solicitud. Es preciso mencionar que las tasas de calentamiento de 200°C por minuto no son únicamente conocidas en la técnica, sino que ni siquiera constituyen tasas de calentamiento muy elevadas en ingeniería. Para demostrar esto, nos permitimos adjuntar una publicación académica de G-f. Xu *et al.* que muestra tasas de calentamiento muy altas (de hasta 4900°C/min) obtenidas por calentamiento con microondas para la producción de óxido de zinc. En este sentido, consideramos que el señor Examinador está equivocado al afirmar que *"no existen procesos evidenciados en el estado de la técnica ni el campo técnico de la ingeniería que permitan tasas de calentamiento de 200°C / minuto, debido a que la cantidad de energía y la cantidad de combustible o material utilizado para el mismo son elevados"*, de hecho, de acuerdo a lo enseñado en la publicación adjunta, las tasas divulgadas en la reivindicación 1 son moderadas. Basados en lo anterior, solicitamos al señor Examinador retirar la objeción por claridad de la reivindicación 1.

En relación a la objeción del señor Examinador respecto a la reivindicación 12, en cuanto dice que *"no determina adecuadamente el rango de tiempo durante el cual se somete la solución de elementos metálicos a calentamiento a una temperatura de 200°C"*, advertimos que la reivindicación 12 es muy clara al establecer el rango que se desea proteger, y que se encuentra debidamente sustentado en la descripción, de 1 minuto a 24 horas. Consideramos que dicho rango es claro y puede ser comprendido sin dificultad por cualquier persona que lea dicha



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reivindicación. No obstante lo anterior, queremos señalar que la descripción presenta catorce (14) ejemplos con condiciones altamente específicas que permiten a un técnico versado en la materia reproducir la presente invención para diferentes configuraciones particulares.

Solicitamos entonces aceptar la totalidad del pliego reivindicatorio, en cuanto el mismo es suficientemente claro y conciso.

2. Novedad

Ahora en cuanto a las objeciones a la novedad de la presente solicitud, en vista del documento WO 03031323 (D1), es preciso mencionar que dicha anterioridad no revela todas y cada una de las etapas del proceso reivindicado.

Para demostrar lo anterior nos permitimos señalar que existen al menos tres diferencias fundamentales entre el proceso de D1 y el de la presente invención, como sigue:

En primer lugar, el proceso de la presente invención requiere específicamente agua en la etapa i), en adición al primer solvente requerido. Por el contrario, la primera etapa del proceso de D1 requiere un solo solvente lo que claramente separa ambos procedimientos.

Por otra parte, notamos que la etapa ii) del proceso de la presente solicitud requiere separar el complejo metal-carboxilato antes de formar la nanopartículas, separación que no se encuentra presente en el proceso de D1.

Contrario a lo enseñado en el proceso de la reivindicación 1 de la presente invención, D1 forma las nanopartículas por descomposición térmica del complejo metálico sin haberlo separado del solvente. La única etapa de separación en D1 es una centrifugación al final del proceso. Adicionalmente, la invención es clara en indicar que se separa el complejo metal carboxilato de una capa orgánica superior, etapa que no es descrita en D1.

Finalmente, el proceso acá reivindicado requiere un segundo solvente seleccionado del grupo conformado por hidrocarburo aromático C₆₋₂₅, éter C₆₋₂₅, hidrocarburo alifático C₆₋₂₅ y amina C₆₋₂₅ (compuestos químicamente diferentes del primer solvente), el cual no se encuentra divulgado en D1. Advertimos que en el recuadro comparativo del examen técnico, el señor Examinador establece que la reivindicación 6 de D1 revela el segundo solvente, lo cual es erróneo. Dicha reivindicación simplemente especifica cuáles son los compuestos químicos que pueden emplearse como el solvente de la primera etapa del proceso de D1.

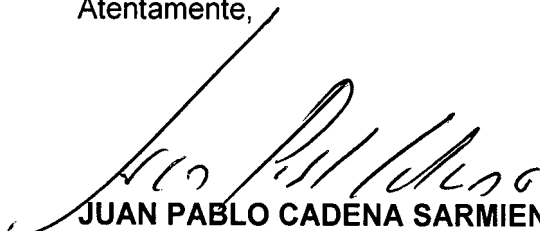
En conclusión, el proceso revelado en la anterioridad D1 no contiene todas las características esenciales de la presente invención, como se definen en la reivindicación 1. Específicamente, al llevar a cabo un examen elemento por elemento de la invención frente a D1, es claro que el proceso reivindicado no se encuentra descrito en D1. En consecuencia, el proceso reivindicado cumple satisfactoriamente con el requisito de novedad.

Anexos

- Xu Geng-fu; Lloyd, Isabel; Carmel, Yuval; Olorunyolemi Tayo; Wilson, Otto. *Microwave sintering of ZnO at ultra-high heating rates. Materials Research Society, Vol. 16, No 10, Oct 2001.*

En vista de lo anteriormente expuesto, respetuosamente solicitamos el retiro de las objeciones de la presente solicitud y la concesión del privilegio solicitado, ya que en opinión del solicitante cumple con todos los requisitos establecidos en la decisión 486.

Atentamente,



JUAN PABLO CADENA SARMIENTO

T.P. No. 57.492 del C.SJ.

C.C. 80.410.337 de Usaquén

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Microwave sintering of ZnO at ultra high heating rates

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In this paper, a unique processing approach for producing a tailored, externally controlled microstructure in zinc oxide using very high heating rates (to 4900 °C/min) in a microwave environment is discussed. Detailed data on the densification, grain growth, and grain size uniformity as a function of heating rate are presented. With increasing heating rate, the grain size decreased while grain size uniformity increased. At extremely high heating rates, high density can be achieved with almost complete suppression of grain growth. Ultrarapid microwave heating of ZnO also enhanced densification rates by up to 4 orders of magnitude compared to slow microwave heating. The results indicate that the densification mechanisms are different for slow and rapid heating rates. Since the mechanical, thermal, dielectric, and optical properties of ceramics depend on microstructure, ultrarapid heating may lead to advanced ceramics with tailored microstructure and enhanced properties.

I. INTRODUCTION

Microstructure is one of the most important factors affecting the properties of ceramics. Density, grain size, pore size, and defects are microstructural characteristics that typically influence behavior. It is generally accepted that a critical issue in microstructure development is the interplay between densification and coarsening. To control microstructure development, parameters such as sintering temperature, sintering time, and heating rate must be optimized and the relationship among densification, grain growth, and pore removal must be understood. Heating rate influences microstructure evolution and densification and thus acts as an important parameter in microstructure control.

Rapid thermal heating, also called fast firing, has been reported to produce beneficial effects such as maintaining relatively fine microstructures compared to slow heating for similar densities.¹⁻³ It is usually performed by the insertion and soaking of a specimen in a preheated high temperature furnace. Brook¹ attributed the superior densification associated with fast firing to rapidly reaching the high-temperature region where densification mechanisms predominate over coarsening mechanisms. Kim *et al.*⁴ pointed out that the advantages of fast firing

include not only finer grain size for a given sintering temperature but also smaller pore size which results from restricted pore growth. Johnson⁵ modeled the effects of heating rate on initial stage sintering of silver and found that at ultrarapid heating rates (e.g., 100 °C/s) the system would pass into intermediate stage sintering with minimal coarsening. García *et al.*⁶ studied fast firing of fine alumina powder and concluded that, besides the densification mechanism mentioned generally for fast firing, transient stresses caused by constrained sintering formed during fast firing play a very important role in the acceleration of densification and the enhancement of a dense, fine-grained microstructure. However, there are some difficulties associated with conventional fast firing.^{7,8} Differential sintering that causes differential densification (nonuniform microstructure, low density or specimen cracking) is one of the problems most often encountered when energy is delivered from the surface to the bulk of the sample by thermal conduction. At sufficiently high heating rates, large temperature gradients can be developed since the sample's thermal time constant is larger than the inverse heating rate. In contrast, microwave sintering, which is characterized by volumetric heating, has the potential to overcome this difficulty.

Microwave processing has earned the attention of researchers pursuing advanced ceramics with potentially unique microstructures and properties currently unattainable by traditional processing.^{9–12} High heating rate is widely recognized as a potential, important advantage of microwave sintering, due to direct, volumetric, instant absorption of microwave power in the sample. Simulation results by Birnboim and Carmel¹³ predicted that, with proper insulation, a heating rate of more than 1400 °C/min is possible during microwave heating of ZnO. Johnson¹⁴ sintered β -Al₂O₃ and Al₂O₃ rods in cold-wall single-mode microwave cavities. The highest average heating rate he obtained is of the order of 50 °C/s, but the estimated peak heating rates were in the range of 100 °C/s. Dé *et al.*^{15,16} used hybrid microwave heating to attain a peak-heating rate of 750 °C/min in pure alumina using a 2.45-GHz multimode applicator. They reported more uniform microstructure and superior properties compared to conventional fast firing for samples processed under similar temperature–time histories. Fang *et al.*¹⁷ successfully used thermal runaway to achieve microwave rapid sintering of hydroxyapatite ceramics with denser microstructure, finer grain size, and better mechanical properties than conventionally sintered materials.

Although microwave heating can, in principle, enable ultrarapid heating, the actual heating rate depends on many factors such as the dielectric properties of materials processed, quality of insulation, temperature measurement techniques, computerized process control, and microwave source capabilities. Only limited success has been reported so far. Good temperature control during rapid microwave heating of ceramics is rare since the heating process is difficult to control. As a result, systematic, reproducible studies of microwave sintering of ceramics at ultrahigh heating rates are not available. Our aim in this study is to close this gap. We achieved a stable, reproducible, ultrarapid microwave heating (URMH) by simultaneously developing a workable high-temperature insulation system and optimizing computer-controlled microwave processing equipment. ZnO was chosen as a model material for URMH studies since it is characterized by a good microwave coupling ($\tan \delta = 0.5$ at room temperature) and a relatively low sintering temperature (1100–1200 °C). In this paper, the results of stable, controlled URMH of ZnO, up to 4900 °C/min, are presented, and the effects of heating rate on densification and grain growth are discussed.

II. EXPERIMENTAL PROCEDURE

All samples were prepared from commercial high-purity ZnO powder (CERAC, Inc., Milwaukee, WI, 99.9% purity, 1.2- μ m median particle size) by uniaxial pressing at 35 MPa in a cylindrical steel die with a diameter

of 2.75 cm, followed by cold isostatic pressing at 300 MPa. All samples had a green density of about 68% of theoretical density and weighed about 20 g.

Microwave heating was performed in atmospheric pressure air using a computerized, highly overmoded 2.45-GHz applicator equipped with an advanced dynamic proportional–integral–differential (PID) feedback loop. The feedback loop continuously adjusts the input power so that the sample temperature closely tracks a preset temperature–time history. The features of the microwave furnace system are the following: a 3-kW, 2.45-GHz magnetron source; water-cooled aluminum applicator with mode stirrer (model 101 of MMT, Knoxville, TN); ports for vacuum and gas feed; microwave safety interlocks; optical temperature measurement (three pyrometers allow temperature to be measured from room temperature to 2500 °C);¹⁸ computer data acquisition; PID temperature feedback algorithm control. The microwave-heating schedule included an initial ramp (usually less than 60 °C/min) from room temperature to 600 °C, followed by heating at specified rate to 1150 °C with variable soaking time. In the previous studies carried out in our laboratory,¹⁹ it was determined that ZnO densification started at about 600 °C, which was a convenient temperature to switch from low temperature to intermediate pyrometer. Therefore 600 °C was selected as the starting temperature to initiate URMH.

Density measurements were performed by the Archimedes method using deionized water as medium. Selected samples were prepared for scanning electron microscopy (SEM) analysis by polishing to 0.05- μ m finish with alumina powder and etching with a 5% HCl solution for 10 s. Grain sizes in the sintered samples were measured by the linear intercept technique described by Mendelson.²⁰ The average grain size, G , was calculated according to $G = 1.56\bar{L}$, where $\bar{L}$ is the measured

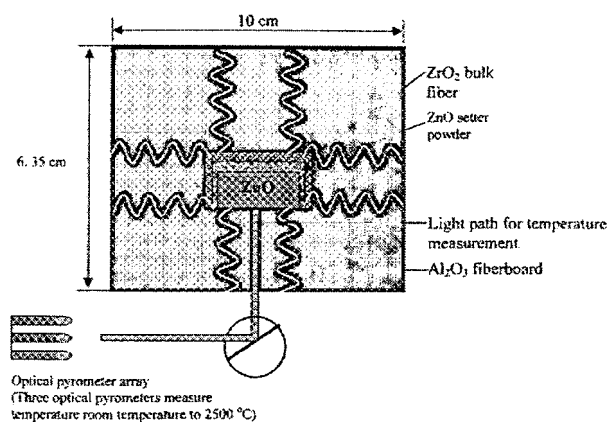


FIG. 1. Schematic diagram of insulation configuration and temperature measurement method used in ultrarapid microwave heating of ZnO sample.

average grain boundary intercept length of a series of random lines on the photomicrographs (more than 300 grains were used for each measurement).

Figure 1 illustrates the insulation arrangement for URMH of ZnO. The alumina fiberboard casket (Zircar, Inc., Florida, NY, Type ZAL-15, 85% Al_2O_3 , 15% SiO_2) was core drilled so its inner diameter is slightly larger than the sample diameter. Inside the casket the sample is covered with a thin layer of ZnO setter powder (3-mm thick) to avoid direct contact with ZrO_2 bulk fiber (Zircar, Inc., Type ZBF) and minimize zinc loss. A small volume of ZrO_2 bulk fiber (4-mm thick) was used between setter powder and alumina insulation.

III. RESULTS AND DISCUSSION

A. Controlled ultrarapid heating using microwave energy

Figure 2 shows that the heating rate was stable, and it was controlled for 1000, 2500, and 4900 $^\circ\text{C}/\text{min}$. The slower heating rates were also at least as stable. This was possible because the feedback control system enabled self-adjustment of the input powder to meet a preset temperature-time scheme using a unique PID algorithm. Figure 3 shows how the input power automatically adjusted to match the sample temperature to the set temperature for a heating rate of 500 $^\circ\text{C}/\text{min}$. The microwave power was continuously adjusted by the computerized feedback loop to minimize the temperature difference

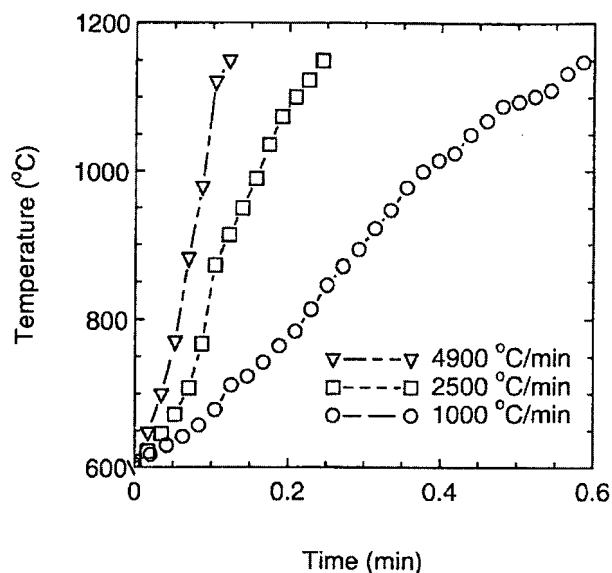


FIG. 2. Measured temperature as a function of time for ultrarapid microwave heating of ZnO samples. Note that rapid heating was initiated at 600 $^\circ\text{C}$ (the "switchover" temperature for our pyrometer array).

between the actual and set temperature. The maximum temperature difference was 56 $^\circ\text{C}$ at 700 $^\circ\text{C}$, and the difference diminished to less than 2 $^\circ\text{C}$ at 1150 $^\circ\text{C}$. Also, it can be seen that only small amount of power (150 W) was required to maintain a sintering temperature of 1150 $^\circ\text{C}$. Figure 4 shows the measured peak input microwave power and total consumed microwave energy as a function of the heating rate. The total consumed microwave energy is evaluated by integrating the recorded real-time input power-time curves. Note that the input peak power increased only by a factor of 2, while heating rate increased by more than a factor of 100. Although higher maximal driving powers were needed for higher heating rates, total microwave energy significantly

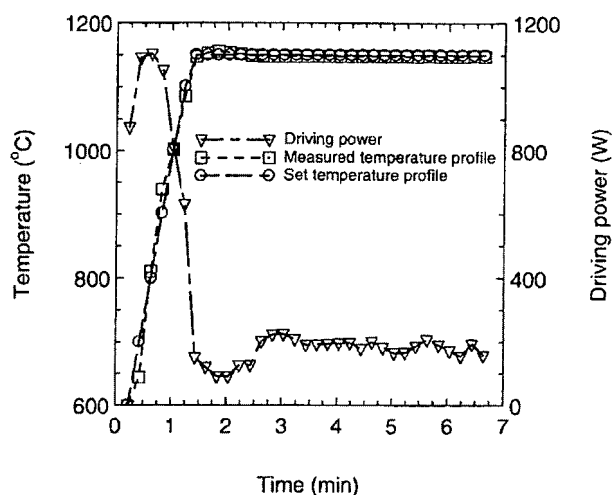


FIG. 3. Measured temperature, set temperature, and driving power versus time for microwave rapid heating of ZnO (500 $^\circ\text{C}/\text{min}$).

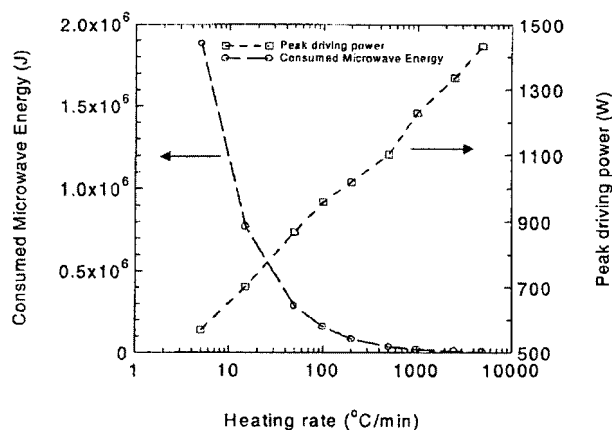


FIG. 4. Measured peak input microwave power and consumed microwave energy versus heating rates for heating of ZnO sample to 1150 from 600 $^\circ\text{C}$. Higher heating rate requires higher peak input power while total energy consumption significantly decreases with the increase in heating rate.

decreased due to shorter heat up periods at higher heating rates. This result is very meaningful for scale up production due to large energy savings and short cycle time at high heating rates.

We found that the critical factors for obtaining stable and controlled URMH of ZnO were proper insulation of sample, the microwave absorption characteristics of the material being processed and computerized process control. In particular, these factors must be addressed simultaneously during microwave processing to achieve controlled ultrarapid heating rates. The first factor, thermal insulation, is very important since it must not only minimize the heat loss from the surface but also help optimize power distribution within the load (that is, optimize partition of microwave power between sample and susceptor, setter powder, etc.). Tian *et al.*'s simulation²¹ indicated that the use of insulation significantly accelerated heating rates. Birnboim and Carmel's¹³ simulation results showed that density and temperature gradients could be reduced if samples are properly insulated. The first factor was satisfied in our experiments by intimately encircling the sample with extremely low thermal conductivity insulation materials (alumina fiberboard and zirconia bulk fiber). The second factor was satisfied by choosing ZnO and starting ultrarapid heating at 600 °C where enhanced dielectric loss allows very good microwave absorption. The third factor was satisfied through both our choice of temperature measurement method and the use of PID control. A noncontact optical pyrometer array was employed to measure the temperature of the bottom surface of the sample since we have found that a thermocouple distorts the local microwave field and limits the heating rate.¹⁸ A dynamic PID control algorithm was used to control the microwave processing power. To avoid temperature overshoot, the PID parameters were determined by running several experiments with dummy samples. This is especially important for achieving stable, controlled ultrarapid heating rates since ZnO absorption is a highly nonlinear function of temperature. The controlled, rapid heating rate of 4900 °C/min, demonstrated in this study, is unimaginable in a conventional furnace. Even in a microwave furnace, such a rapid heating rate can lead to thermal runaway, unless the furnace is equipped with the features described.

The ZrO₂ bulk fiber insulation in Fig. 1 was included for two reasons. First, its thermal conductivity is extremely low [0.1 W/(m K) at room temperature] so it is an excellent thermal barrier. Second, in couples well above 400 °C and, thus, can be used to enhance microwave heating. In experiments without ZrO₂, it took 3–5 min for ZnO to respond to microwave irradiation and begin to heat. The addition of an appropriate amount of ZrO₂ bulk fiber greatly reduces the microwave response time of the sample, typically to 5–10 s for ZnO. In addition, the auxiliary heating provided by the ZrO₂ fiber

appears to provide more uniform heating than insulation without ZrO₂ fiber or susceptor arrangement with a SiC ring.

B. Microstructural uniformity at ultrahigh heating rates

Microstructural uniformity during microwave processing, especially at high heating rates, is a concern since heat loss from the surface can lead to temperature gradients. Temperature gradients may limit the acceptable heating rate since large temperature gradients cause differential shrinkage, cracking, and inhomogeneous microstructure. As emphasized earlier, a good insulation design that minimizes surface heat loss will alleviate temperature gradients. Dadon *et al.*²² studied temperature gradients in nonisothermal microwave processing of ZnO (with a heating rate of 15 °C/min) using thermocouples for differential temperature measurements. They found that a temperature difference between core and surface only existed at lower temperatures and that this difference diminished to zero when the sintering temperature of 1100 °C had been reached. In the present experiments, optical pyrometers were employed to monitor temperature at the center region (6.35-mm spot diameter) of the bottom surface of the ZnO sample and microstructural observations were employed to trace the temperature history inside the sample. Most microstructural observations were done on the lower surface after 2 mm had been polished away to eliminate surface effects. To verify that the microstructure was uniform, cross-sectional analyses were also done using fracture surfaces.

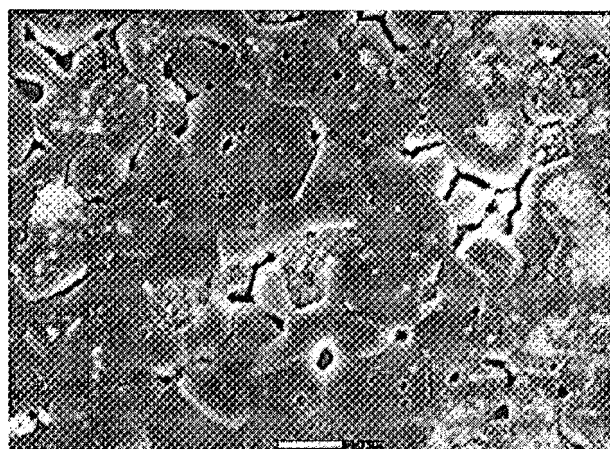
Figure 5 shows representative microstructures for ZnO samples heated to 1150 °C at 50 and 2500 °C/min and then held for 5 min. Limited inter- and intragranular porosities are present in both samples. Figure 6 shows the measured grain size as a function of position from center to edge within the cylindrical ZnO samples. One can see that, for the heating rates of 5 and 50 °C/min, the grain size decreases slightly from the center to the surface. This indicates that temperature gradients existed in the samples. At heating rates above 200 °C/min, the grain size is uniform. The uniformity of grain size indicates that the temperature gradients are substantially reduced during high heating rates. Similarly the grain size was uniform throughout the thickness of the samples indicating that there were no significant vertical temperature gradients. Here the absence of a grain size gradient is taken as evidence that there were no substantial temperature gradients. Also shown in Fig. 6 is the inverse relationship between grain size and the logarithm of the heating rate. This indicates that the heating rate can be used to continuously control the grain size. This is very

important since the mechanical, optical, electrical, and thermal properties often depend strongly on the grain size.

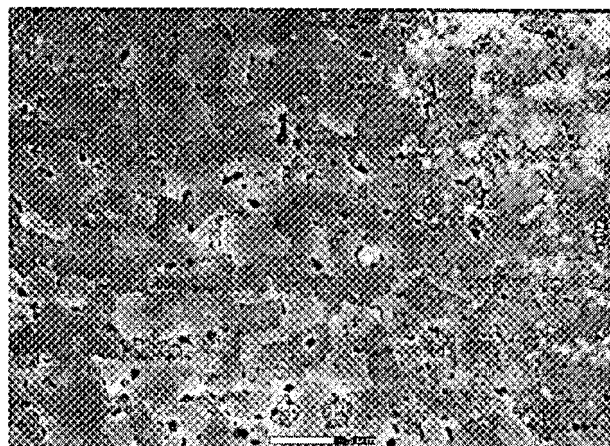
C. Effect of heating rate on densification in ZnO

The effect of heating rate on densification in ZnO was examined by measuring the densities of samples at different temperatures for different heating rates. The results summarized in Fig. 7 indicate that heating rate strongly affects the densification process and final density. Each data point in this figure is the average of two separate samples. After the samples were heated to the indicated temperatures, the power was switched off immediately and the sample was cooled naturally. Then the density was determined by dimensional measurements. The densities of all samples heated to 1150 °C were at least 94% TD, and the densities of the slowly heated

samples were higher than those of the rapidly heated samples. This was expected since there was little time for densification at the fastest heating rates. Our results



(a)



(b)

FIG. 5. SEM micrographs showing the microstructure of ZnO microwave sintered at 1150 °C for 5 min for various heating rates: (a) 50 °C/min; (b) 2500 °C/min.

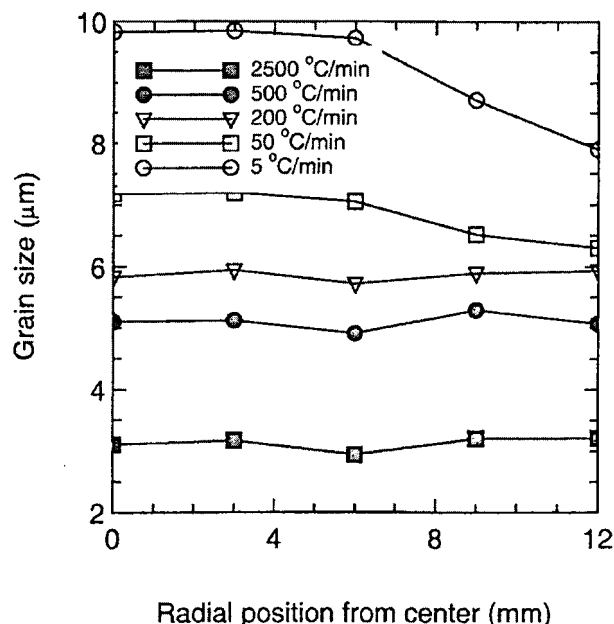


FIG. 6. Measured grain size versus position in a cylindrical ZnO sample, microwave processed at various heating rates. Samples were heated to 1150 °C and held for 5 min.

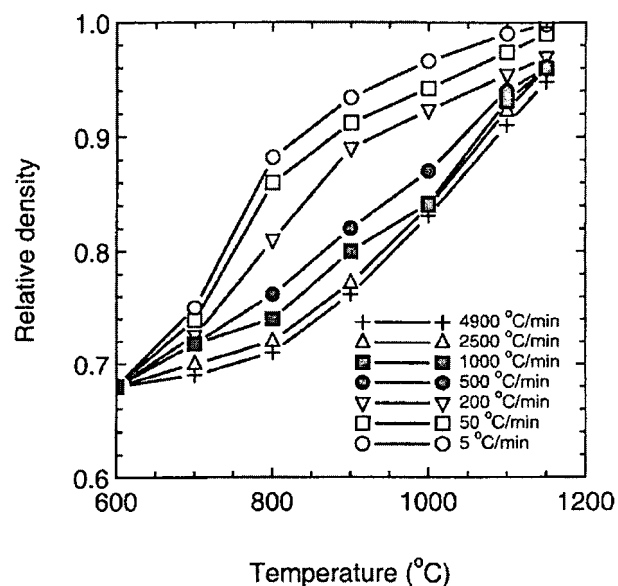


FIG. 7. Relative density versus temperature for ZnO samples (green density = 68% TD) sintered at heating rates between 5 and 4900 °C/min. All samples are microwave heated to the corresponding temperatures without holding. All data points are averaged from two separate samples. Note that densification rate is higher by more than 3 orders of magnitude for 4900 °C/min compared to 5 °C/min at a sintering temperature of 1150 °C.

agree with those of Chu *et al.*²³ and Demartin *et al.*,²⁴ although they did not sample such a wide range of heating rates.

In Fig. 7, the densification curves for heating rates up to 200 °C/min, as would be expected, have the familiar sigmoidal shape often seen in conventional pressureless sintering and are shifted to higher temperature with increasing heating rates. However, for faster heating rates between 500 and 4900 °C/min, the densification curves are different. Unlike the slow heating rate curves, they are concave, with little densification below 800–900 °C. This lag in densification is probably due to a lack of time for densification. Although densification appears sluggish for the higher heating rates during the heat-up period, once densification begins, the densification rate is much larger (10^3 magnitude of order) than that for lower heating rates as can be simply calculated from Fig. 7.

In Fig. 5(b), the ZnO sample (98.2% TD) sintered at 1150 °C for 5 min at a heating rate of 2500 °C/min shows a microstructure with equiaxed grains. The intergranular pores are almost-spherical pores. This microstructure fits the classical geometry described in the final-stage sintering models. During final-stage sintering, the densification rate, can be expressed in the following form:^{25,26}

$$\frac{dp}{dt} = \frac{C\gamma_s DN_g}{G^n}, \quad (1)$$

where ρ is density, C is a constant, and γ_s is the solid/gas surface energy; D represents either the lattice diffusion coefficient (D_L) or the grain boundary diffusivity ($\delta_b D_b$), where δ_b is the grain boundary width and D_b is the grain boundary diffusion coefficient, N_g is the number of boundary pores per grain, and G is the grain size. In the model, the grain size exponent, n , is 3 for lattice diffusion control and 4 for grain boundary diffusion control. It is evident from Eq. (1) that densification rate will increase when $\delta_b D_b$ (or D_L) is increased or G is decreased. Since all samples are originally identical, they should have an identical $\delta_b D_b$ or D_L at the onset of densification at 600 °C. Thus, we believe that the observed higher densification rates at higher heating rates are a result of strongly suppressed grain growth.

Figure 8 shows relative density as a function of sintering time at 1150 °C for different heating rates. For short sintering times (≤ 5 min), samples with lower heating rates have higher densities than those with higher heating rates. After 5 min of soaking at 1150 °C, the densities were similar for all the heating rates. Densities $\geq 98\%$ of theoretical were consistently obtained for all heating rates after a 5-min hold at the sintering temperature. The data for any heating rates are reproducible to within $\pm 1\%$. This indicates the major densification process is essentially completed in about 5 min, even for a heating rate of 4900 °C/min. Longer sintering time

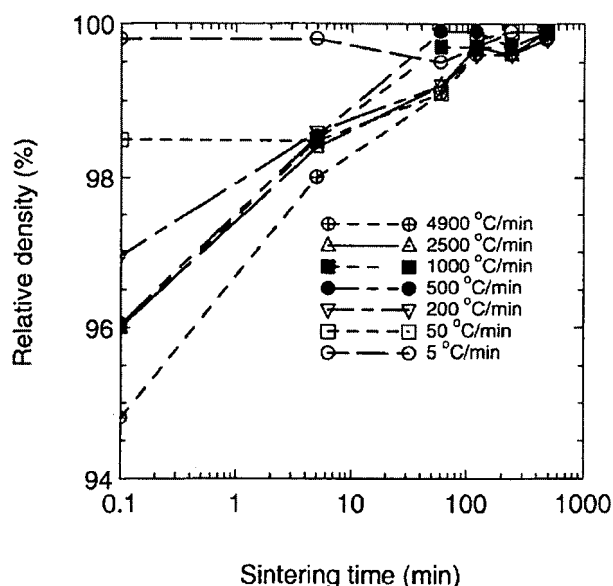


FIG. 8. Sintered density of ZnO as a function of sintering time at 1150 °C with different heating rates. The experimental data were fitted using the polynomial $\log(t + 0.1)$, where time t was measured in minutes.

produces similar density independent of heating rates. These results demonstrate that comparable densities can be obtained for the microwave sintering of ZnO over a very broad range of heating rates.

D. Grain growth of ZnO at high heating rates

Figure 9 shows the measured dependence of the average grain size of ZnO on the sintering time at 1150 °C for different heating rates. The grain size increases with sintering times and decreases with the increasing heating rates. Also the grain growth curves have different slopes implying differences in grain growth behavior. Figure 10 shows representative microstructures for samples sintered for 480 min with heating rates of 5 and 500 °C/min, respectively. As noted in the previous section, the microstructures were uniform. Small pores are present inside the grains in all samples, but there are more intragranular pores in the sample with higher heating rates.

Figure 11 shows grain size–density trajectories for different heating rates. The grain size–density (G – ρ) trajectory is a function of the relative ratio of the densification rate to the grain-growth rate. The flattening of the G – ρ trajectories observed at the high heating rate (>200 °C/min) indicates that ultrahigh heating rate enhances densification over grain growth (coarsening). As expected, most of the grain growth occurs during the final stages when the porosity decreases below about 5%.

Grain growth during sintering has been argued to be driven by the size and, thus, chemical potential differences between grains. Attempts to densify ceramics

without, or with, very limited grain growth during pressureless sintering, even during conventional fast firing, have been unsuccessful.^{6,7} This is because of considerable grain growth always accompanied the densification. By considering the thermodynamics of the sintering process, Lange^{27,28} pointed out that grain growth, either for intermediate stage or final stage sintering, was a necessary condition for continuous densification during sintering. Traditionally, the isothermal rate of grain growth can be expressed by the phenomenological kinetic grain growth equation:

$$G^n - G_0^n = k(T)t \quad (2)$$

where G and G_0 are the grain sizes at holding time t and $t = 0$ and n and $k(T)$ are constants for a particular grain growth mechanism. This equation was derived for dense materials, where grain growth is the result of grain boundary motion with $n = 2$ or 3 .^{25,26} It is also thought to be applicable to porous materials in the intermediate and final sintering stages.²⁹ For constant heating rate, Eq. (2) becomes

$$G^n - G_0^n = \frac{k_0}{\alpha} \int_{T_0}^T \exp\left(\frac{-Q}{kT}\right) dT \quad (3)$$

assuming that $k(T) = k_0 \exp(-Q/kT)$ and $T = T_0 + \alpha t$, where k_0 is a constant, Q is the activation energy for grain growth, and k is Boltzman's constant. G^n should be inversely proportional to the heating rate, α . When α is large enough, G will be nearly equal to G_0 . This means that almost no grain growth will occur. For pure ZnO, a

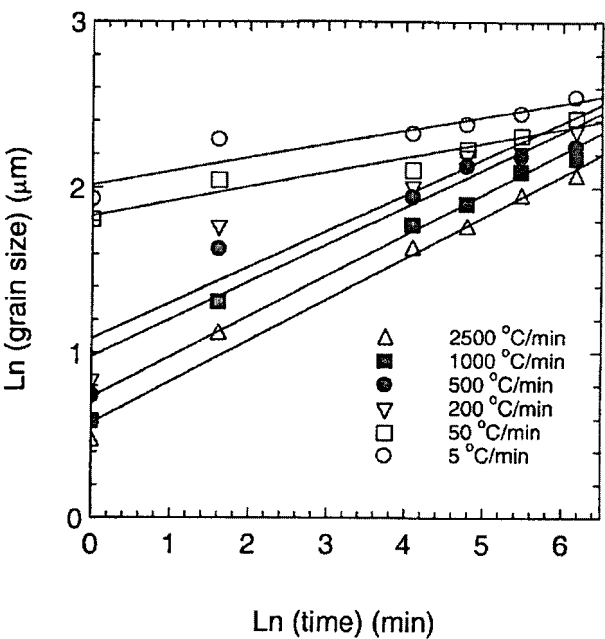


FIG. 9. Grain growth behavior of ZnO versus sintering time at 1150 °C under different microwave heating rates.

grain growth activation energy of approximately 224 KJ/mol and a preexponential constant or $\log k_0$ value of approximately 13 have been reported.^{30,31} Using these values, $G^n - G_0^n$ is almost 0 when $\alpha = 4900$ °C/min. This fits our experiments where the grain in the samples with 4900 °C/min only grew from 1.2 to 1.4 μm for no hold (94% TD) or 2.8 μm for 5-min hold (98%).

In this investigation, grain growth exponent (n) values appeared to vary with the heating rates. At heating rates below 50 °C/min, the slopes are equal to 1/12, yielding a grain growth exponent of 12, while, at heating rates between 200 and 2500 °C/min, the slopes are equal to 1/5, yielding a grain growth exponent of 5. Varying n values indicates different grain growth mechanisms existed and dominated during sintering under different heating rates. It is difficult to experimentally identify which mechanism is controlling grain growth during sintering since densification and pore morphology evolution occur simultaneously. It is suggested in this study that heating

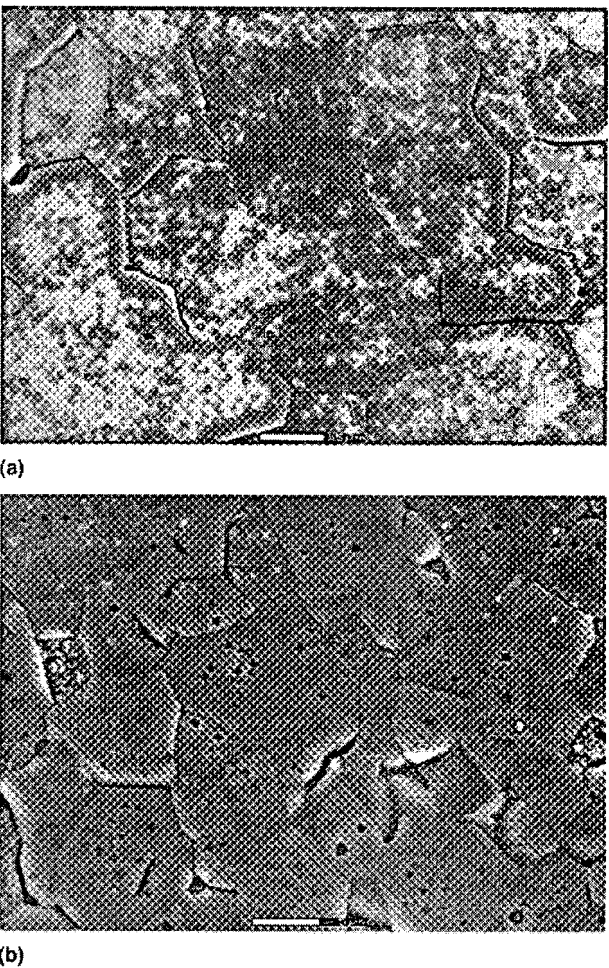


FIG. 10. SEM micrographs of polished and etched surfaces of microwave sintered ZnO at 1150 °C for 480 min: (a) 5 °C/min; (b) 500 °C/min. Densities and grain sizes are given in Figs. 8 and 9.

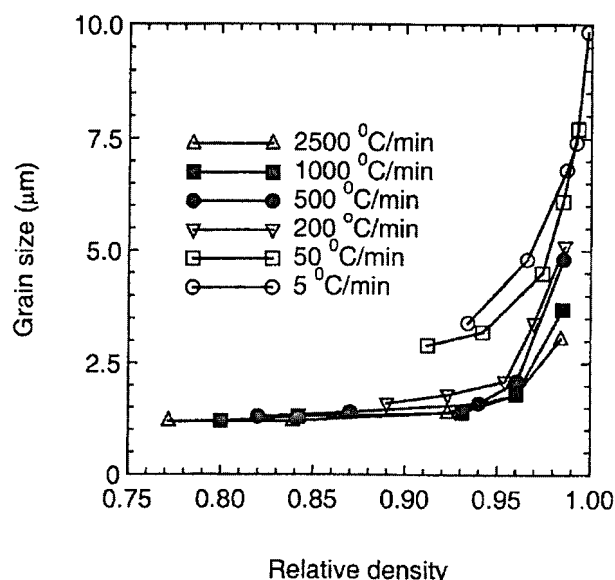


FIG. 11. Grain size–relative density trajectory of ZnO microwave sintered under different heating rates.

rate changes the relative contributions of surface, grain boundary, and lattice diffusion during the sintering process, which, in turn, are responsible for the differences in grain growth processes. A lower grain growth exponent at higher heating rates might be a result of contributions from other physical processes taking precedence over grain boundary migration.

The mechanisms for coarsening and densification have long been a focus of sintering studies. It is generally accepted that sintering occurs by competition between densifying mechanisms and coarsening mechanisms. At very high heating rates, the sample reaches high temperature within seconds bypassing nondensifying mechanisms which are active at relatively low temperatures. Our results indicate the following: (1) Densification at high heating rates mainly takes place at higher temperatures. (2) Grain growth occurs primarily after sintering temperature is reached. (3) Heating rate appears to have a strong effect on grain growth even after samples are densified. Thus, by modification of the heating rate, significant control can be exerted over the mass transport mechanisms, microstructure evolution, and final microstructure.

Finally, one may question whether microwave effects plays a role in the grain growth suppression reported in this paper. Microwave effects can be unambiguously identified by comparing conventional and microwave processing of ZnO under similar conditions. In this study all the data are based on microwave sintering. We could not find results on such ultrahigh heating rates in conventional furnace to compare to. The difficulty is that conventional very rapid and relatively uniform heating

can only be achieved for very small samples (where the heating rate is smaller than the inverse of the thermal time constant of the sample being processed). In the absence of such data it is difficult to ascribe the observed effects as microwave effects.

IV. CONCLUSIONS

Stable, controlled, ultrahigh heating rates have been demonstrated in microwave sintering of ZnO. This is made possible due to a combination of good insulation design, consideration to power distribution within the load, localized optical temperature measurement to minimize heat loss, and computerized control of the sintering process. It was found that ultrahigh heating rates (500–4900 °C/min) could produce more uniform microstructures than slower heating rates. Very rapidly fired samples have different densification behavior from slowly heated samples: Ultrarapid microwave heating results in enhanced apparent densification rates for ZnO compared to slower microwave heating. Grain size drastically decreased with increased heating rate. Grain growth exponents of 12 and 5 were respectively obtained for slow heating rates and ultrarapid heating rates implying that grain growth mechanisms might be different for slow and ultrarapid heating. These results are very promising with respect to obtaining controlled, tailored microstructures in ceramics. They may lead to the retention of nanostructure in nanopowder materials.

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