DIFFUSION-CONTROLLED PROCESSES IN MICROWAVE-FIRED OXIDE CERAMICS *

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ABSTRACT

Processing oxide-based ceramics using microwave heating leads to a number of unexpected results, which can only be interpreted in terms of enhanced diffusion. Enhanced sintering has been observed in alumina and zirconia. Accelerated grain growth in dense, hot-pressed alumina has been demonstrated. Increased diffusion coefficients have been observed for diffusion of oxygen in sapphire. As yet, a satisfactory theory to account for these phenomena has not been developed. This paper reviews the experimental work conducted at the Oak Ridge National Laboratory during the past four years on the processing of oxides in both 2.45 and 28 GHz microwave furnaces.

INTRODUCTION

Microwave processing enhances numerous kinetic processes in oxide ceramics. Enhanced sintering has been demonstrated in high-purity alumina [1,2,3], 94% alumina [4], zirconia [5], and alumina-zirconia composites [6]. The rate of densification is generally enhanced over that of coarsening during sintering such that a finer grain size after sintering is obtained in microwave-fired ceramics as compared to conventionally-fired ones [2,5]. Accelerated grain growth in dense, hot-pressed, high-purity alumina has been demonstrated [7,8]. As will be reported in this paper, diffusion of oxygen in single crystal sapphire is also enhanced in the microwave field; to the best of our knowledge, this is the first report of direct evidence for enhanced diffusion in a ceramic single crystal by a microwave field. The phenomenology of microwave processing of ceramics has been well documented in terms of enhanced sintering and annealing effects. However, at present there does not exist a satisfactory theory of why the microwave field acts to enhance these diffusion-controlled processes. Current indications are that the electric field is important; furthermore, there is some limited evidence for the existence of an effect of frequency on some kinetic processes.

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EXPERIMENTS IN SINTERING, GRAIN GROWTH, AND DIFFUSION

Enhanced sintering in alumina was the first phenomenon that was observed in our studies of microwave processing of oxide ceramics. This means either sintering at a lower temperature, or sintering faster at the same temperature, for microwave processing as compared to conventional processing. Fig. 1 shows a typical sintering curve for microwave (28 GHz) and conventional sintering of high-purity alumina in terms of sintered density vs temperature (50°C/min heating rate, with a 1 h hold)[1]. There is an obvious acceleration of densification for the microwave case. Depending on where in the sintering cycle one looks, there is a 300-400°C differential in the sintering curves. Furthermore, there is a significant difference in the shape of the sintering curves; in the microwave case, density increases much faster with temperature than it does in the conventional one. The microwave-sintered samples pass through the first and second stages of sintering faster than do the conventionally sintered ones. This is reflected in the final dense part; the grain size of the microwave-sintered samples is much finer than that of the conventionally sintered ones.

Additional experiments on sintering of high-purity alumina were conducted to determine the rates of sintering as a function of temperature [2]; from these data, an apparent activation for sintering was obtained. Samples were sintered for times ranging from 5 to 120 min, at temperatures of 950, 1000, and 1100°C in the 28 GHz microwave furnace and at 1250, 1300, and 1350°C in a conventional furnace. Fig. 2 shows a standard Arrhenius plot for the sintering rate (at 80% theoretical density) vs 1/T, where T is the temperature in degrees Kelvin. The activation energy observed for conventional sintering, 575 kJ/mol, is similar to that reported by other investigators for diffusion-controlled processes in alumina [9,10]. In contrast, the activation energy for microwave sintering, 160 kJ/mol, is only 1/3 that for conventional sintering, and is without precedent in the ceramic sintering literature. The mechanism that is responsible for enhancing the sintering of alumina to such an extent is not known. The presence of the electric field in the microwave furnace is surely a factor. The particular frequency that is employed may also be a factor. Recently, Bykov and Goldenberg [11] reported an activation energy of ≈100 kJ/mol for sintering of alumina at 82 GHz. Their work provides confirmation of the reduced activation energy for sintering by microwave processing. It also suggests that there may be a frequency effect for diffusional processes in the microwave furnace. Their experiments were conducted at almost 3 times the frequency at which our experiments were conducted, and the activation energy that they reported is even lower than that which we reported in 1987 [2], 100 vs 160 kJ/mol.

Not only is the rate of sintering affected by microwave firing, but also the evolution of microstructure during sintering [2]. Figure 3 shows that the evolution of pore size distribution is different for microwave and conventional firing. The pores in the microwave fired samples tend to stay more "open" to a later stage in sintering than
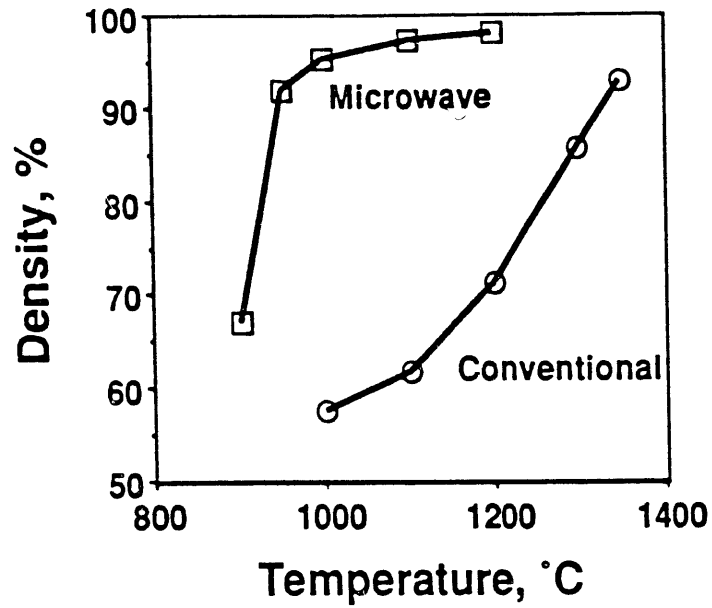
Figure 1. Microwave sintering of high-purity alumina (Sumitomo AKP50) greatly accelerated densification relative to conventional sintering.
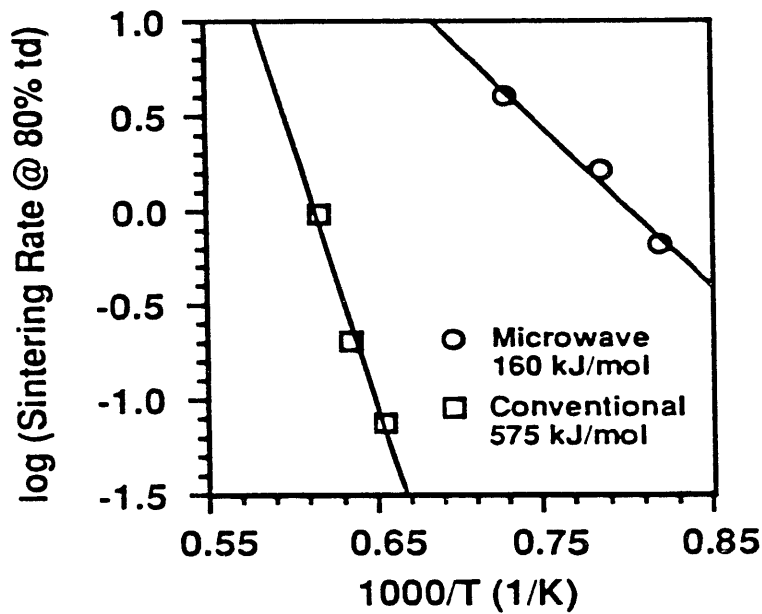

Figure 2. The apparent activation energy for sintering of high-purity alumina was lower for microwave firing than for conventional firing.
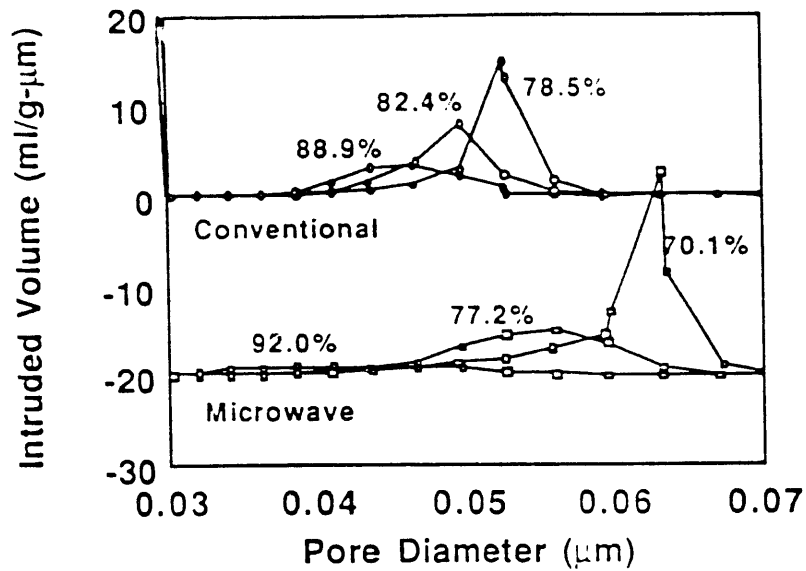
Figure 3.Pore size evolution was different for microwave and conventional firing of high-purity alumina. Numbers are sintered densities in percent. Microwave intruded volumes are shifted by 20 ml/g-μm.
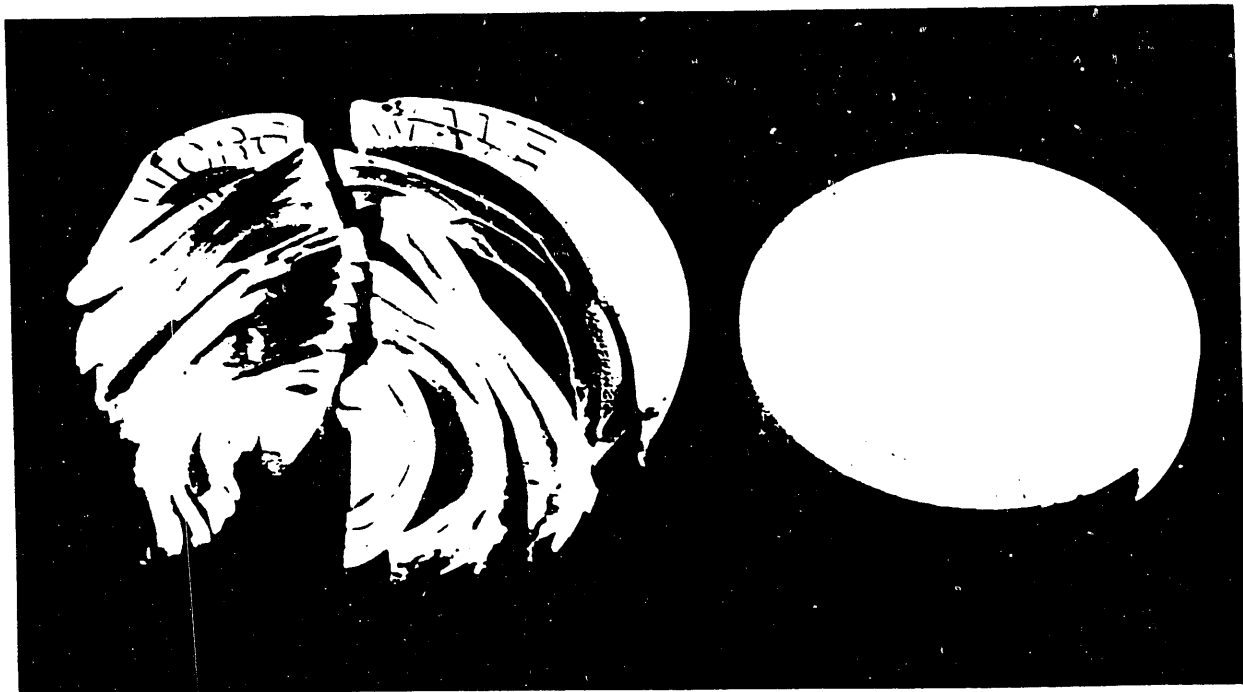

Figure 4. Successful microwave sintering of zirconia (Tosoh TZ3Y, ZrO$_2$-3 mol % Y$_2$O$_3$) requires a uniform furnace: a) low uniformity furnace; b) high uniformity furnace.

do those for conventional firing. The result is a reduction in the grain size for the microwave fired materials. It is hypothesized that there is an enhancement of bulk or grain boundary diffusion over surface diffusion in the case of the microwave fired samples that leads to the differences in pore evolution and final grain size. No adequate theoretical basis exists for interpreting these data. Also note that because the path of sintering is different in the microwave and conventional cases, the comparison of activation energies for sintering in the two cases is not a true comparison; there are structural differences as well as kinetic differences, and the comparison is really between two very different processes.

Accelerated sintering has also been demonstrated in zirconia at both 2.45 and 28 GHz. Sintering of zirconia at 28 GHz proceeded in a manner similar to that for alumina. A composition of ZrO_2 - 3 mol % Y_2O_3 was sintered to full density at 1200°C in 1 h, Fig 4b; conventional firing of this composition required a temperature of ≈1500°C to achieve full density. There was a differential of 300°C in the firing temperatures for microwave and conventional sintering, which is similar to the effects found for sintering alumina at 28 GHz. Sintering of zirconia at 2.45 GHz was significantly more challenging [5]. The nonuniformities that exist in our untuned, 2.45 GHz furnace (nominal dimensions 20 in. diam x 30 in. long) lead to the formation of "hot spots" in the zirconia parts, which in turn produced nonuniform sintering. Zirconia is especially susceptible to the formation of "hot spots" because its dielectric properties change rapidly with temperature and it has an extremely low thermal conductivity. A striking example of "hot spot" formation and its consequences is shown in Fig. 4a and demonstrates the need for uniform heating in the processing of zirconia. The formation of "hot spots" was eliminated through the use of a "picket fence" arrangement [5] to provide indirect heating of the zirconia at low temperature. The picket fence enabled us to produce parts that were crack free at 2.45 GHz. Fig 5 shows the sintering behavior of ZrO_2 - 8 mol % Y_2O_3 at 2.45 GHz using the "picket fence" arrangement; a heating rate of 3.5°C/min was used to attain temperature, and a 1 h hold was employed. The sintering curve for microwave firing is shifted ≈150°C from that for conventional firing confirming the existence of a "microwave effect" for the sintering of zirconia at 2.45 GHz. As was observed in the sintering of alumina at 28 GHz, Fig. 1, the density of the microwave fired samples increased much faster with temperature than did the conventional ones. This suggests that the activation energy for sintering of zirconia at 2.45 GHz might be lower in the microwave case than in the conventional case. The grain size of the final dense zirconia is finer in the microwave-fired samples than in the conventional samples (conventional: $T_{sinter}=1375$°C, $\rho=99.35\%$ td, $d=3.5$ μm; microwave: $T_{sinter}=1200$°C, $\rho=99.47\%$ td, $d=2.2$ μm). Again, this behavior is similar to that observed for alumina.

The sintering experiments have demonstrated the existence of a "microwave effect" in both alumina and zirconia; however, because sintering involves numerous
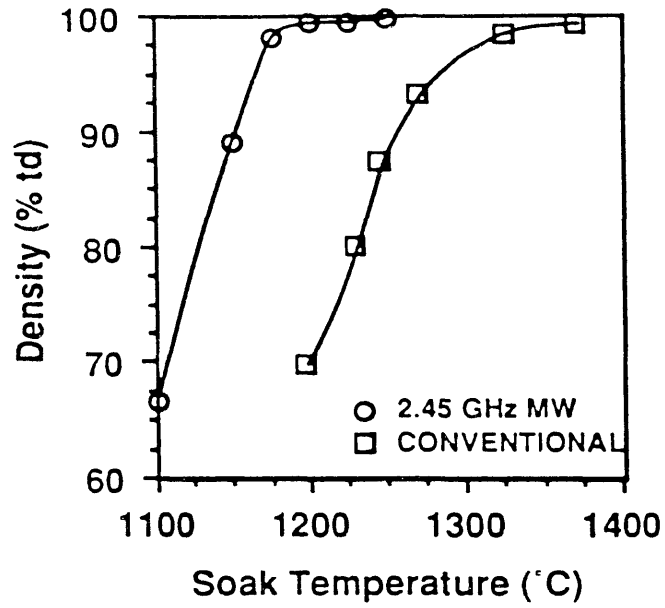
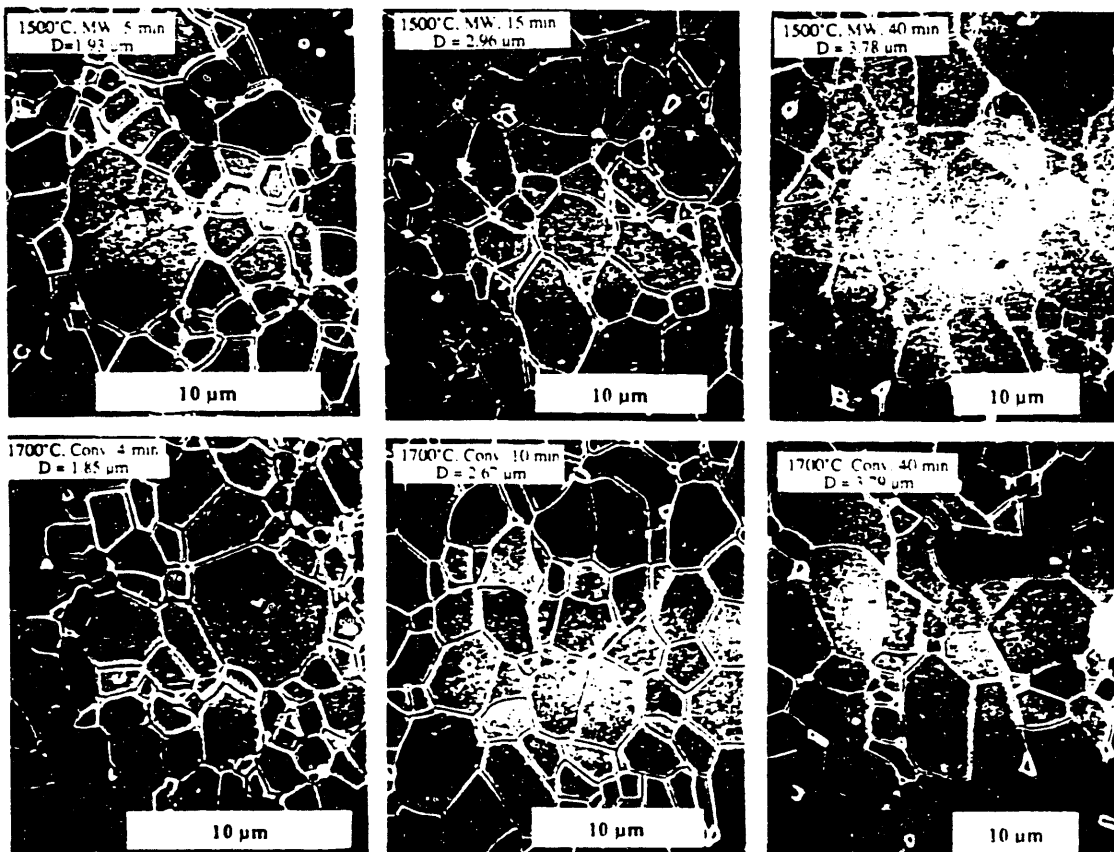Figure 5. ZrO2 - 8 mol % Y2O3 exhibited enhanced sintering at 2.45 GHz using the "picket fence" arrangement.

Figure 6. Grain growth was structurally similar for microwave and conventional annealing. Hot pressed Reynolds RCHP; starting grain size, 1.1μm.

diffusion mechanisms, it is difficult to be definitive about the differences in the rates of the processes. It was decided to examine grain growth in dense, hot pressed alumina [7] because it is simpler. Fine grained ($\approx$1.1 μm) starting material was synthesized by hot pressing. Anneals were conducted in a conventional vacuum furnace and in the 28 GHz microwave furnace, also under vacuum. Fig. 6 shows that microstructural development during grain growth proceeded in a similar manner for both the conventional and the microwave anneals. A detailed quantitative analysis of the microstructures [8] demonstrated that there were no differences in the structural evolution of the grains in either case; only the kinetics were different. Both the conventional and the microwave annealed samples showed cubic grain growth kinetics, Fig. 7. Cubic kinetics are to be expected for alumina based on literature data [12-15]. The rate of grain growth was greatly accelerated in the microwave case; e.g., the kinetics at 1500°C in the microwave case are the same as they are at 1700°C in the conventional case. The activation energy for the process was determined by plotting the slopes of the cubic grain growth curves against 1/T in a standard Arrhenius plot, Fig. 8. The activation energy for microwave grain growth was $\approx$20% lower than that for conventional grain growth, 480 vs 590 kJ/mol. This is significantly different than the results that were obtained for sintering, in which the activation energy for microwave sintering was only 1/3 of that for conventional sintering, 160 vs 575 kJ/mol. The smaller difference in activation energy for grain growth as compared to sintering reflects the fact that the grain growth process is structurally the same in both cases, whereas the sintering process for microwave and conventional sintering are quite different. The differences in activation energy for grain growth are more representative of the differences in diffusion processes in the two cases, whereas the differences in activation energy for sintering reflect both diffusional and structural differences.

To further investigate the differences in diffusion-controlled processes between microwave and conventional firing of ceramics, a series of tracer diffusion experiments was performed. The substrate for the experiments was single crystal sapphire (alumina). It was chosen because we had demonstrated accelerated sintering and grain growth in alumina. The diffusing species chosen was ^{18}O. Initially we had considered using hetero-cations such as Ni^{+2} or Cr^{+3} as the diffusing species; these choices would have made the analysis of the diffusion profiles relatively easy because we could have used electron microprobe x-ray analysis. However, these tracers were abandoned because of concerns regarding differential coupling of the microwaves to the regions of the crystal that were rich in the Ni^{+2} of Cr^{+3}; this might result in preferential heating of those regions and bias the diffusion results. ^{18}O did not cause such concerns. The ^{18}O tracer was deposited on the sapphire substrate by electron beam evaporation from an ^{18}O-enriched alumina source to a thickness of $\approx$1500A. Parallel annealing experiments were conducted in the 28 GHz microwave furnace at 1500, 1550, 1575, and 1600°C and in a conventional furnace at 1700, 1750, and 1800°C. Concentration depth profiles were determined by proton
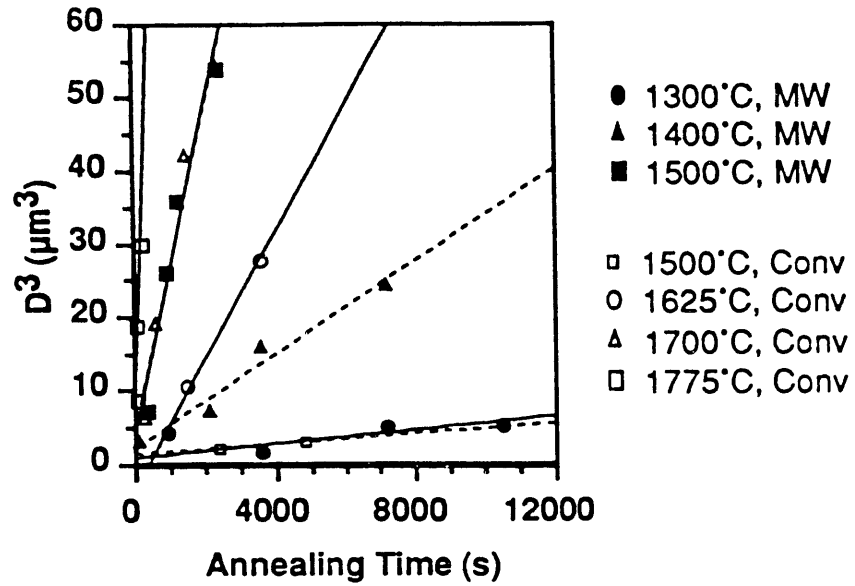
Figure 7. Grain growth in hot-pressed alumina-0.1 wt% MgO followed cubic kinetics for both microwave and conventional anneals.
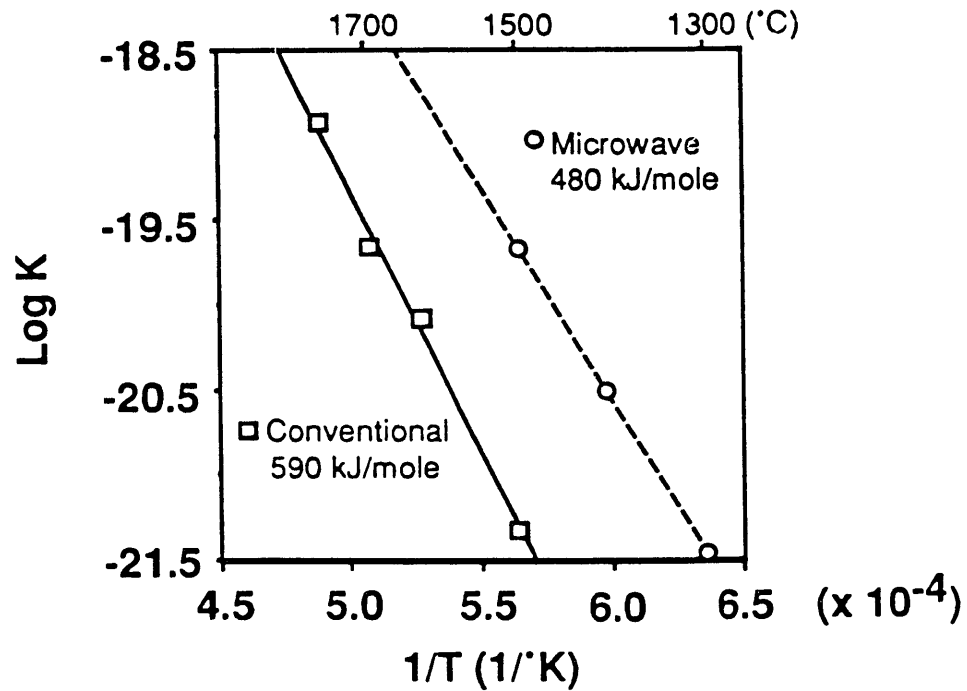

Figure 8. The activation energy for grain growth in alumina - 0.1 wt % MgO was lower for microwave annealing than for conventional annealing.

activation analysis using the 5 MeV Van der Graff accelerator at the Oak Ridge National Laboratory. The thin film solution to the diffusion equation was used to determine the diffusion coefficients from the concentration profiles. Because the diffusion coupons were small (10x10x0.3 mm), a ballast/crucible arrangement [7] had to be used. In this arrangement a large crucible with lid (~150g total weight) is made that has the same composition as the small samples that are to be run (in this case Sumitomo AKP50 99.99% alumina). The small samples are placed in a cavity in the crucible. On exposure to the microwave field, the sample becomes part of the total load in the furnace. In this way, we can effect coupling to the small sample that is equivalent to that achieved in a large sample.

There was a large increase in the diffusion rate of ^{18}O in the microwave case as compared with the conventional case. Fig. 9 shows two typical diffusion concentration profiles: microwave at 1600°C, and conventional at 1800°C. The concentration profile for the microwave case is much better developed than the one for the conventional anneal. The slope of the curves is inversely proportional to the diffusion coefficient, and shows that the diffusion coefficient for the microwave case is higher than for the conventional case, even though the microwave annealing temperature is 200°C lower. A more complete picture is given in Fig. 10, where the diffusion coefficients for both cases are plotted in an Arrhenius diagram. The activation energy for diffusion in the microwave anneals is about 40% lower than that for the conventional anneals, 410 kJ/mol vs 710 kJ/mol. The 710 kJ/mol value for conventional diffusion is typical for literature values.[16, 17] This is the first time that a "microwave effect" has been reported in a single crystal ceramic; all other reports have been for either sintering of powders or annealing of polycrystalline samples. The existence of a "microwave effect" in the single crystal demonstrates that there is some kind of bulk crystal interaction between the ceramic and the microwaves, and that neither free surfaces nor grain boundaries are necessary to produce accelerated kinetics in the microwave field.

DISCUSSION

We have observed accelerated sintering in alumina and zirconia by microwave processing as compared with conventional processing. For alumina, there is a drastic reduction in the apparent activation energy for sintering, from 575 to 160 kJ/mol, which has since been confirmed by Bykov and Goldenberg [11]. There are differences in the evolution of microstructure in microwave and conventionally processed alumina, which lead to a finer grain size in the microwave-fired material. For zirconia, enhanced sintering has been demonstrated at both 2.45 and 28 GHz. It is suggested that the "microwave effect" for sintering might be stronger at the higher frequency, although this effect is not yet definitive. The rate of grain growth in dense, hot pressed alumina is 1-2 orders of magnitude higher in the microwave case than in
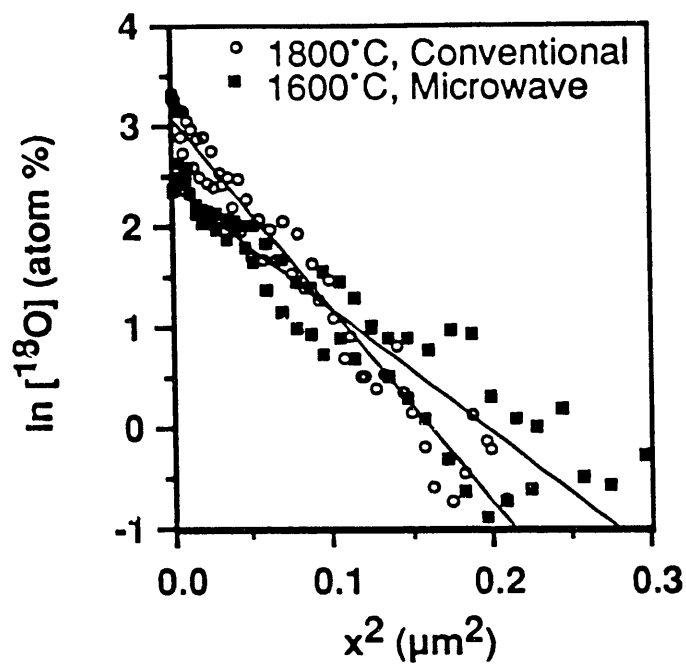
Figure 9.   Diffusion of ^{18}O into sapphire occurred faster for microwave heating than for conventional heating.
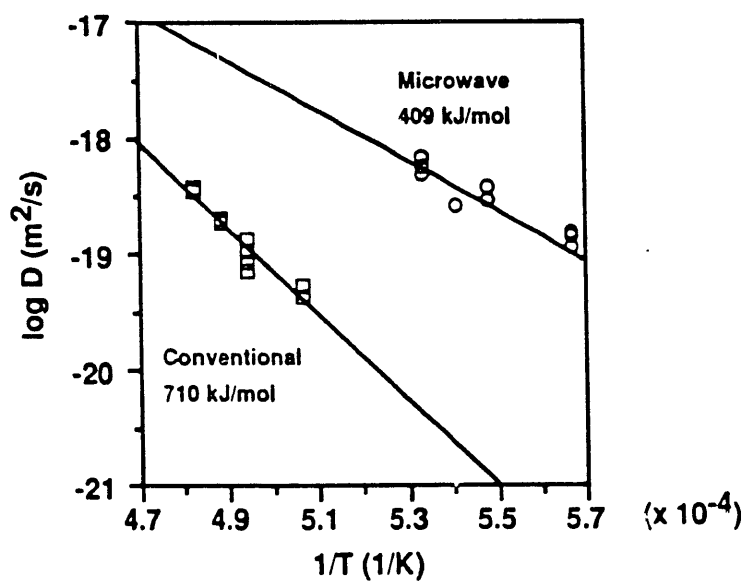

Figure 10.   The activation energy for ^{18}O diffusion in sapphire was lower for microwave annealing than for conventional annealing.

the conventional case, depending on temperature. The activation energy for grain growth is reduced from 590 to 480 kJ/mol by microwave annealing. A "microwave effect" has been demonstrated for diffusion of ^{18}O in single crystal sapphire; at a given temperature, diffusivities are increased by ≈ 2 orders of magnitude. The activation energy for ^{18}O diffusion is reduced from 710 to 410 kJ/mol, which is in fairly good agreement with the reduction observed for grain growth, but is much lower than the reduction observed for sintering. This is the first report of a "microwave effect" in a single crystal ceramic.

The 40% reduction in activation energy for diffusion in sapphire is in better agreement with the reduction in activation energy that was observed for grain growth in alumina ($\approx 20\%$) than the reduction that was observed for sintering in alumina ($\approx 300\%$ reduction). These differences again reflect the fact that in sintering, there are differences both in the structural evolution of the process in microwave and conventional cases as well as in the kinetics of the processes. In contrast, for diffusion and grain growth, the structural processes are essentially the same for both conventional and microwave annealing.

Based on the observations reported above, one may appropriately ask the question - what is the current state of understanding of these microwave phenomena? There are three basic working hypotheses regarding the origin of these microwave phenomena that will be examined in turn:
1. Free surface effects, as exist in plasma sintering.
2. Grain boundary coupling.
3. Coupling to lattice defects and other bulk crystal effects.

As regards free surface effects such as those in plasma sintering, Johnson [18] has shown that both atmosphere and processing path are critical to the development and maintenance of the plasma. For example during vacuum processing, if the plasma is established and then allowed to be extinguished, it cannot be re-established. This is because the plasma initially couples to surface hydroxyl groups which are stripped off during the initial heating. Also in plasma processing, the composition of the processing atmosphere is critical to the successful firing of the material. In contrast, in microwave processing, the process of heating can be repeatedly interrupted and restarted with no adverse effects. Furthermore, the processing atmosphere has little effect on the ability to heat and sinter a particular material.

Grain boundary coupling could be important in the sintering of materials in the microwave furnace. This might be especially true as regards the relative enhancement of grain boundary, volume and surface diffusion. Grain boundary coupling might also be important in terms of the distribution and action of additional phases in two and three phase materials.

Coupling to lattice defects and other bulk crystalline effects have been shown to be important based on the diffusion results reported herein. The sapphire diffusion experiments demonstrate that there is need for neither free surfaces nor grain boundaries to develop a "microwave effect." Therefore, one must look for either an effect between the microwaves and the crystal lattice, or preferential coupling of the microwaves with point defects. Unfortunately, at the present time no effective theory of the interactions of microwaves with crystalline ceramics exists to guide our thinking in these areas.

SUMMARY

Microwave firing accelerates a number of kinetic processes in oxide ceramics and can change the path of microstructural evolution during sintering. Densification can occur at 150 to 400°C lower in a microwave furnace as compared with a conventional furnace. The grain size after sintering can be finer in the microwave-fired materials. The apparent activation energy for sintering is reduced by 2/3 for alumina. Grain growth kinetics in dense, hot-pressed alumina are shifted ≈200°C by annealing in the 28 GHz microwave furnace as compared with conventional annealing; the activation energy for grain growth is reduced by ≈20%. Diffusion in single crystal alumina is accelerated by microwave annealing at 28 GHz; diffusion rates are increased by two orders of magnitude. The activation energy for oxygen diffusion is lowered by ≈40%. Finally, the mechanisms by which these diffusion-controlled processes are enhanced are not known at this time. However, electric field effects on crystal lattice dynamics are indicated.

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