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MICROWAVE (HYBRID) HEATING OF ALUMINA AT 2.45 GHZ: II. EFFECT OF PROCESSING VARIABLES, HEATING RATES AND PARTICLE SIZE

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Microwave (hybrid) heating (MHH) is a novel combination of microwave (MW)-material interaction and conventional radiant/conduction mechanisms that facilitates the attainment of very high heating rates in a 2.45 GHz. multimode MW cavity. Dry-pressed green samples of pure, undoped alumina were fired under similar conditions by MHH and conventional fast firing (CFF). The effect of processing variables (temperature, time) and heating rates on MHH and CFF were investigated. The effect of particle size on the MHH phenomena was also studied. MHH has been shown to result in accelerated densification (higher densification to coarsening ratios) relative to CFF under the same conditions of temperature and time. Higher heating rates with MHH result in higher densities and smaller grain sizes. Smaller starting particle sizes with MHH also culminate in the highest densities and the largest grain sizes similar to conventional firing.

INTRODUCTION

Fast firing of ceramics and the consequent microstructural benefits in terms of higher densities and smaller grain sizes has been the subject of extensive research [1-3]. The higher densities and smaller grain sizes were attributed to a rapid transition to higher temperatures which caused a suppression of surface diffusion and other 'coarsening without densification' mechanisms that exist at lower temperatures[3]. At higher temperatures, the predominance of the mechanisms of grain boundary and lattice diffusion that cause densification, lead to rapid sintering and densification with little or no coarsening.

The use of MW energy for the sintering of ceramics, although a relatively new development, has seen a proliferation of activity in recent times. The potential of microwaves for the firing of ceramics at lower temperatures, and with smaller grain sizes compared to conventional sintering techniques, have been demonstrated unequivocally [4-8]. This has been attributed to higher diffusion and a lower activation energy for sintering that is characteristic of MW energy[4,6]. However, although the use of MW energy for sintering serves to accelerate the process, preheating the material to the critical temperature at which it starts to couple efficiently with the microwaves is still a problem, especially at the low frequency of 2.45 GHz. Longer times are spent in heating up the sample to the critical temperature range above which MW-material interaction and consequently, rapid heating occurs readily. This, as well as the higher diffusion rates that are associated with MW heating, may be the reason for the appreciably higher grain sizes (with microwaves) reported in a recent study on the 'comparison of conventionally fast fired and MW fired alumina'[9].

In order to apply the benefits of fast firing to MW sintering, a technique that makes use of both MW-material interaction as well as conventional radiant/conduction heating mechanisms has been developed. 'Hybrid heating using MW energy' [10-13] makes use of radiant/conduction heating to rapidly heat samples through low temperature regimes to a critical temperature above which the microwaves couple readily with the material. A peak heating rate of 750°C per minute for pure, undoped alumina in a 2.45 GHz, 6.4 KW(max.) multimode cavity, making use of less than half the peak power output, has been attained. Advantages of this technique over CFF, in terms of significant enhancements in the homogeneity of the microstructure and improved mechanical properties (under the same sintering conditions), have been demonstrated [10-13].

EXPERIMENTAL PROCEDURE

Two grades of pure, undoped alumina were employed. Type1(designated A-16)[*] was a 99.97% pure alumina grade (as received) with an average particle size of 0.48 microns, a very broad particle size distribution, and a surface area of 4.697 m^2/g. This was used for a study of the effect of processing variables (time, temperature) on specimens sintered by MHH and CFF, under the same state conditions. Type 2[**](designated AKP-15, 30, 50) was a very high purity (>99.99%) undoped alumina, and comprised 3 grades of varying particle size distributions, and average particle sizes and surface areas of 0.68μ(3.5 m^2/g), 0.39μ (7.5m^2/g), and 0.23 μ (10.9 m^2/g) for AKP-15, AKP-30 and AKP-50, respectively. These were used to study the effect of particle size on the MHH phenomena.

However, for the study on the effect of heating rates on MHH, the AKP-50 grade of ultra-pure alumina powder was used after rendering it free from hard aggregates by ultrasonication and centrifugal sedimentation. The average particle size of the AKP-50 powder dropped from 0.23 μ (as-received) to 0.19 μ after processing. The hybrid heated samples were sintered under the same state conditions of temperature and time, with only a variation in the heating rates.

The experimental set-up for the MHH has been described and illustrated elsewhere [10,13]. MHH was effected in static air in a 2.45 GHz, 6.4 KW (max)[***] multimode cavity, with the sample enclosed in a silicon carbide lined susceptor. Temperature monitoring was effected by inconel shielded 'K'-type thermocouples[#](for temperatures up to 1100°C) and by two color infrared pyrometry[##] (for temperatures above 1100°C). A peak heating rate of the order of 1500°C in 120 sec (750°C per minute) for pure undoped alumina at a power output of around 3 KW was attained.

CFF (conventional fast firing/ isothermal sintering) was effected in static air by inserting the samples into a resistance heated tube furnace[+] which was preheated to the sintering temperature. The samples were stationed in alumina boats which in turn, were slowly inserted into the hot zone of the tube furnace. Temperatures were read off a 'B' type Pt-Rh thermocouple [#](with digital display) which was kept in contact with the alumina boat and the walls of the alumina tube of the furnace.

Bulk and relative densities of the sintered samples were obtained by the Archimedes density method. The samples were then polished using standard ceramographic techniques. Samples sintered at 1000, 1200, 1300 and 1400°C were thermally etched at 995, 1195,1290 and1390°C for 3,3,3 and 2 hours, respectively. The

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[*] Aluminum Company of America (Alcoa) Inc., Pittsburgh, PA.

[**] Sumitomo Chemical America Inc., New York, N.Y.

[***] Model Radarline QMP 2101B-6, The Raytheon Company, Waltham, MA.

[#] Omega Engineering Inc., Stamford, CT.

[##] Ratio Scope 8, Capintec Inc., Fair Lawn, N.J.

[+] Model Sola-Basic, Lindberg, Watertown, WI.

samples sintered at 1500°C were etched at 1450°C for 1 hour. Microstructures representative of both the surface and the interior of each sample were obtained in the SEM.

Grain intercept lengths and porosities were computed from the SEM micrographs using standard quantitative stereological techniques. Average grain sizes were determined from measured average lineal grain intercept lengths according to the equation [3]

$$\text{grain size} = 1.56 \bullet \text{grain intercept length} \qquad (1)$$

The resulting data were plotted, correlated and compared .

RESULTS AND DISCUSSION:

Effect of Processing Variables on the Sintering of A-16 Alumina: Microwave (Hybrid) Heating vs. Conventional Fast Firing.

Identical green samples were sintered using MHH and CFF at 1300, 1400, 1500°C, with holding times of 15, 30 , and 60 minutes at each temperature.

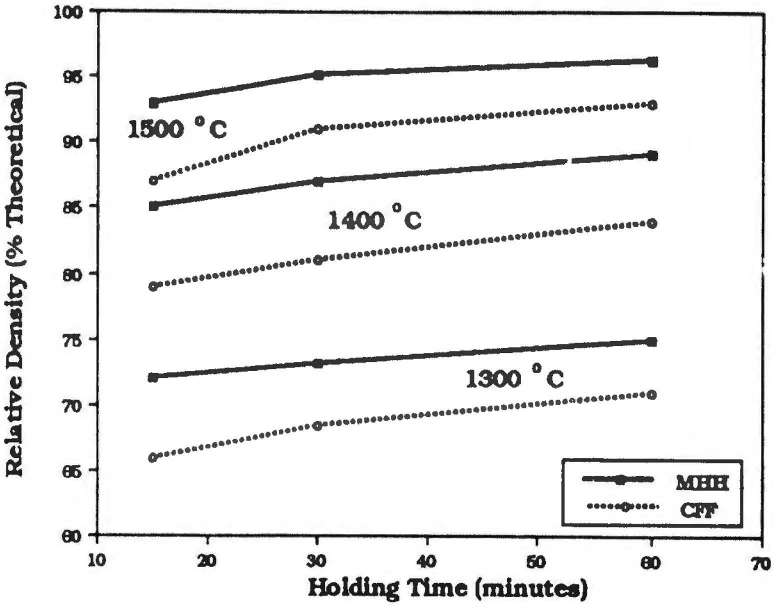
Figures 1(a) and 1(b) are plots of the relative density and densification rate against holding time, respectively. Densification rates were computed from the Fig. 1(a) by normalizing the plots with respect to the starting green density, and plotting the slopes of the 3 line segments (from each line) against time, to yield Fig. 1(b). The densification rates for MHH at each temperature and time were appreciably higher than those for the CFF. This is consistent with the results reported by Janney et al. [4,14], and Tian et al. [5], and the enhanced densification may be ascribed to the increased diffusion rates attributed to MW energy- the 'MW effect' [14]. One other factor that may be partly responsible is the higher temperature (temperatures 50-80°C in excess of the sintering temperature) experienced by the interior of the MHH samples relative to the specimens sintered by CFF [13].

Figures 1(c) and 1(d) are plots of the average grain intercept (GI) size and grain growth rate (microns per minute) as a function of the holding time, respectively. Although the MHH samples displayed somewhat larger grain sizes than the CFF samples, the disparity in grain sizes was minimal, and almost comparable. This is a significant improvement over the results reported sometime earlier in a similar study, [9] making use of MW energy alone for the sintering process. The appreciably smaller grain sizes for the MHH samples in our case may be attributed to the faster heating rates --the culmination of both MW-material interaction and conventional radiant/conduction mechanisms that contribute to the densification process. This is a pointer to the fact that there is indeed a heating rate effect on the MHH phenomena, as will be discussed in the following section. The somewhat larger grain sizes with MHH, relative to CFF can be attributed to three reasons. Recent work by by Janney et al. [14,15] has demonstrated that the activation energy for grain growth with microwave energy is about 20 % lower than that for conventional sintering (480 vs. 590 kJ/mol). Besides this, the higher temperatures at the interior of the MHH sample [13], as well as the preferential interaction of the microwaves with the porosity [7] also serve to accelerate densification as well as grain growth.

An interesting aberration in the form of a dramatically higher GI size was shown by the CFF sample that was sintered at 1500°C for 60 minutes. There was anomalous grain growth and pore coarsening at the center of the sample. The reasons for this anomaly are not well understood.

Figure 1(e) is a plot of the average grain size versus relative density, normalized with respect to the sintering temperature. From this graph, and those for the densification and grain growth rates (Figures 1(b) and 1(d)), it is evident that MHH yields significantly higher densities, with comparable or somewhat larger grain sizes (a higher densification to coarsening ratio) relative to CFF, under the same conditions of time and

1(a)



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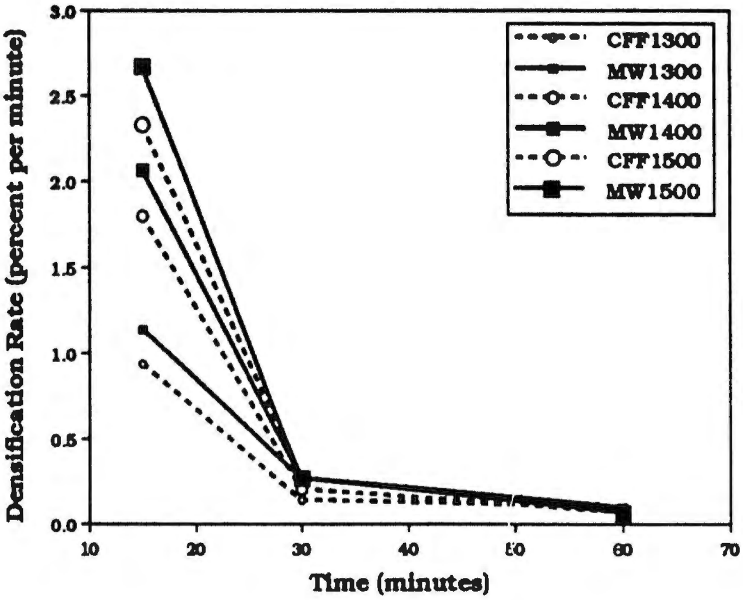
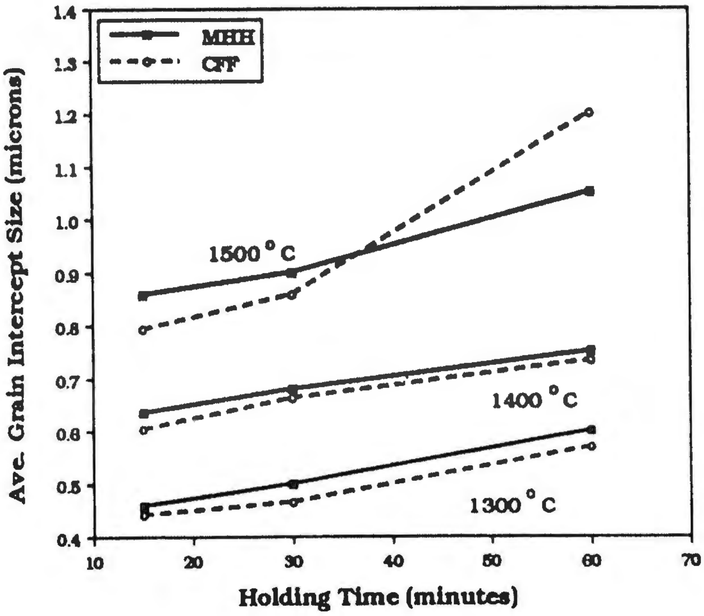


Figure 1. Effect of processing variables (temperature, time) on the sintering of A-16 alumina: MW (hybrid) heating vs. conventional fast firing.
(a) Relative Density vs. Holding Time
(b) Densification rate vs. Holding time

1(c)



1(d)

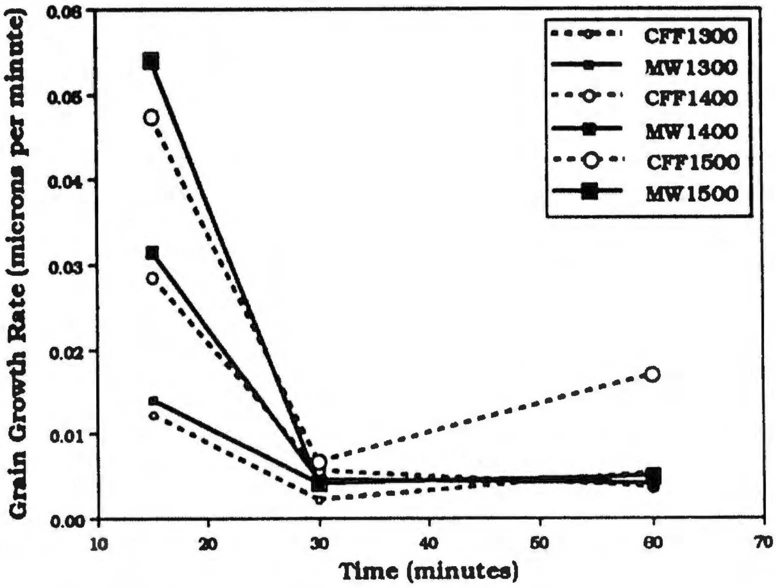


Figure 1. (Cont'd.) Effect of processing variables (temperature, time) on the sintering of A-16 alumina: MW (hybrid) heating vs. c onventional fast firing.
(c) Average Grain Intercept (GI) Size vs. Holding Time
(d) Grain Growth Rate vs. Holding Time.

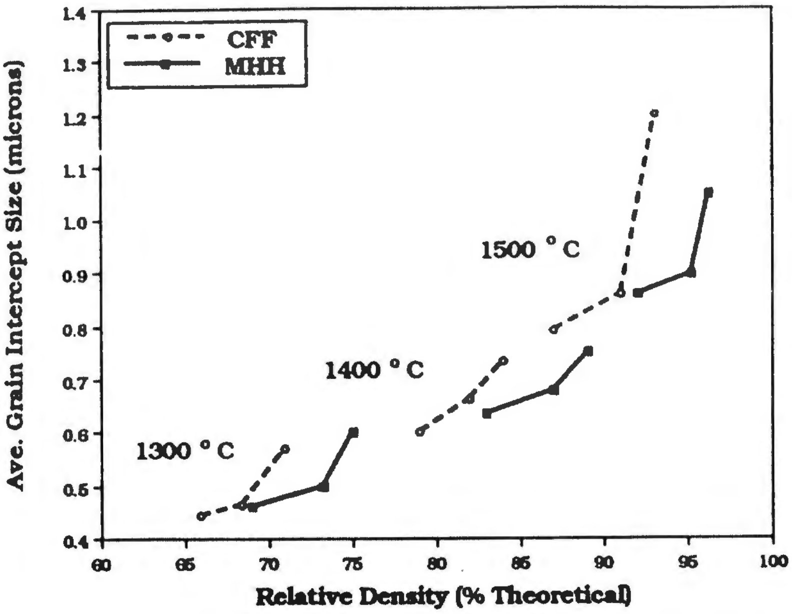


Figure 1. Effect of processing variables (temperature, time) on the sintering of
(Cont'd.) A-16 alumina:: MW hybrid heating vs. conventional fast firing
(e) Average Grain Intercept (GI) Size vs. Relative Density

temperature. The fact that the densification rates for MHH are significantly higher than the grain growth rates relative to CFF, are consistent with results reported by Janney et al. [15], which suggest that the difference in activation energies between MW and conventional sintering for densification (160 versus 575 kJ/mol, respectively) are far higher than the difference in activation energies for grain growth (480 versus 590 kJ/mol, respectively). These results clearly show evidence of accelerated sintering and densification occurring in the MHH specimens relative to the CFF samples.

Effect of Heating Rates on the Sintering of AKP-50 Alumina: MW (Hybrid) Heating vs. Conventional Fast Firing:

For this set of experiments a more reactive (fine) powder and a better green microstructure (free of aggregates and agglomerates) was desired, so that any differences in the MHH phenomena, owing to variation in heating rates alone, would be evident. The ultrapure, ultrafine (~0.23 μ) undoped AKP-50 alumina powder was chosen. This was rendered free of hard agglomerates by ultrasonication and centrifugal sedimentation. The average particle size after processing dropped to 0.19 μ. Identical dry-pressed green samples (6 gm) were then sintered at 1500°C for 15 minutes by MHH, using heating rates of 750, 375, 150 and 62°C per min, and also by CFF (heating rate-1500°C per min).

Figures 2(a) and 2(b) are plots of the relative density and grain intercept (GI) size, respectively, versus heating rate (°C per min).The GI sizes were computed as an average of GI sizes from the surface and the interior of the specimens. Although the CFF sample was sintered using the highest heating rates (1500°C per min), the MHH samples sintered at heating rates of 375, and 750°C per min had higher densities (97.8 and 95.7 versus 95.4 for the CFF sample). Also, the GI size for the 750°C per min MHH sample was the lowest,

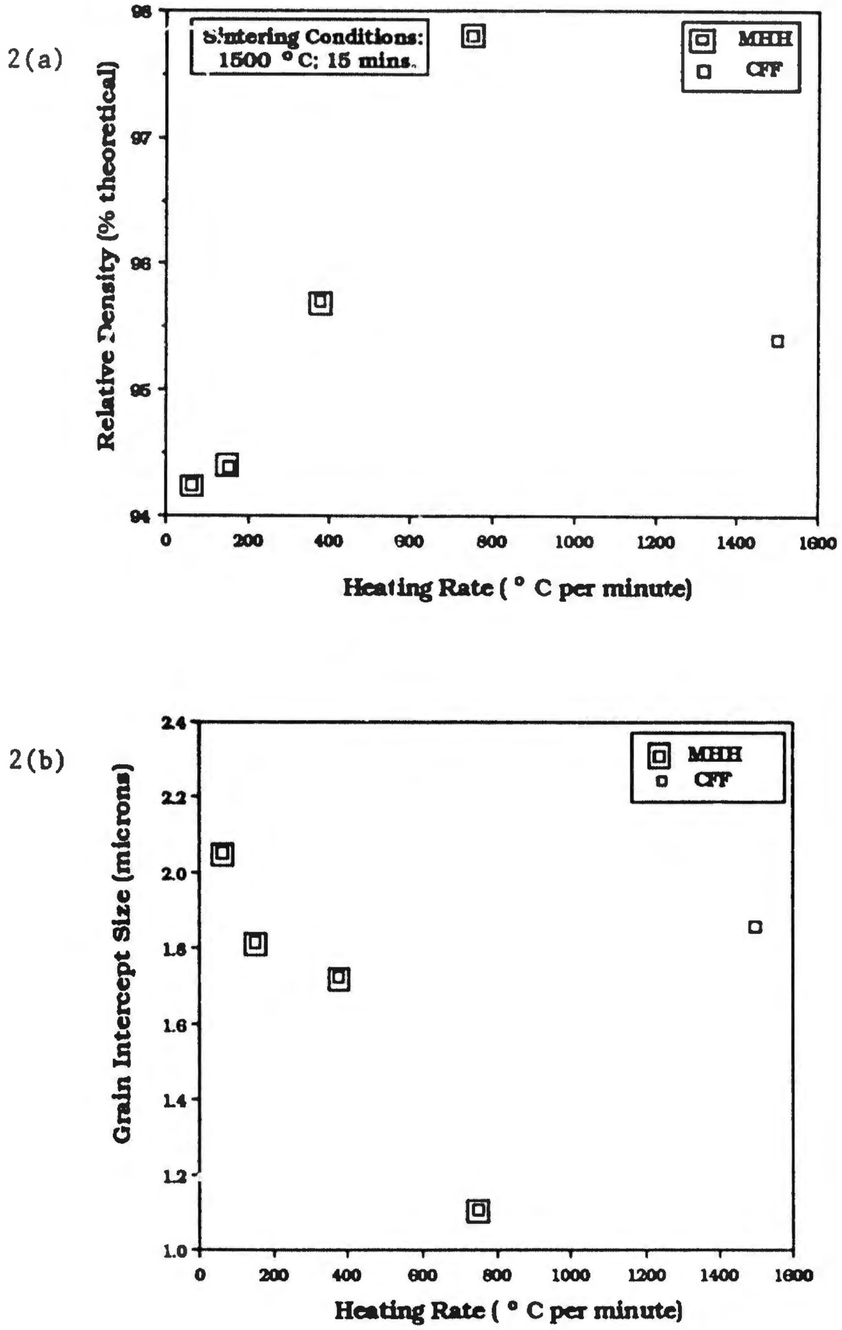


Figure 2. Effect of heating rates on the sintering of AKP-50 alumina: MW (hybrid) heating vs. conventional fast firing.
(a) Relative Density vs. Heating Rate
(b) Average Grain Intercept (GI) size vs. Heating Rate.

and that for the 62°C per min MHH sample was the highest. The CFF sample had a GI size intermediate between those of the 150°C per min and 62°C per min MHH specimens.

These results show evidence of the influence of heating rates on the MHH phenomena, relative to CFF. Although the CFF sample was sintered using the highest heating rates, the higher density and lower GI sizes for the samples sintered by MHH using appreciably lower heating rates is a pointer to the enhanced diffusion process accredited to MW energy. It can be concluded that for the samples sintered by MHH at the high heating rates of 375 and 750°C per min, densification is enhanced at the cost of coarsening, relative to the CFF sample. This is due to the fact that these specimens make a very rapid transition through the lower temperature range where surface diffusion-controlled coarsening predominates, to the higher temperatures where the densifying mechanisms of lattice and grain boundary diffusion are predominant. This results in higher densities and smaller average grain sizes (higher densification to coarsening ratios) relative to the CFF sample. For the samples sintered by MHH at the heating rates of 62 and 150°C per minute, it can be surmised that the densification to coarsening ratio is comparable or lower than that for the CFF specimen.

Effect of Particle Size on the MW (Hybrid) Heating of AKP Alumina:

The particle size distributions of the three AKP powders and the sintering cycles employed are illustrated in figures 3(a) and 3(b), respectively. Sintering was carried out at temperatures ranging from 1000° - 1500°C in the 2.45 GHz MW oven with a constant holding time of 30 minutes, under hybrid heating conditions.

The post sintered relative densities and resulting grain sizes are illustrated in figures 3(c) and 3(d), respectively. Grain sizes for the samples sintered at 1000°C and 1200°C could not be computed accurately owing to incomplete densification and problems encountered with thermal etching.

The trends observed for the samples sintered at 1400°C and 1500°C are pretty much analogous to those known for conventional sintering. Smaller starting particle sizes, and consequently larger surface areas result in higher densities, and larger grain sizes, owing to a higher driving force for sintering, densification, and grain growth.

CONCLUSIONS

MW (hybrid) heating facilitates the attainment of perhaps the highest possible heating rates (750°C per minute) attainable with pure, undoped alumina in a 2.45 GHz, multimode MW cavity.

MHH results in accelerated densification (higher densification to coarsening ratios) as compared to CFF, when sintered under the same state conditions of temperature and time.

MHH is significantly influenced by heating rates, in a manner similar to conventional sintering. Higher heating rates result in higher densities and smaller grain sizes.

The influence of particle size on the MHH phenomena is analogous to conventional sintering. Smaller starting particle sizes culminate in the highest densities and largest grain sizes. This may be attributed to the higher surface area, and consequently, higher driving force for sintering.

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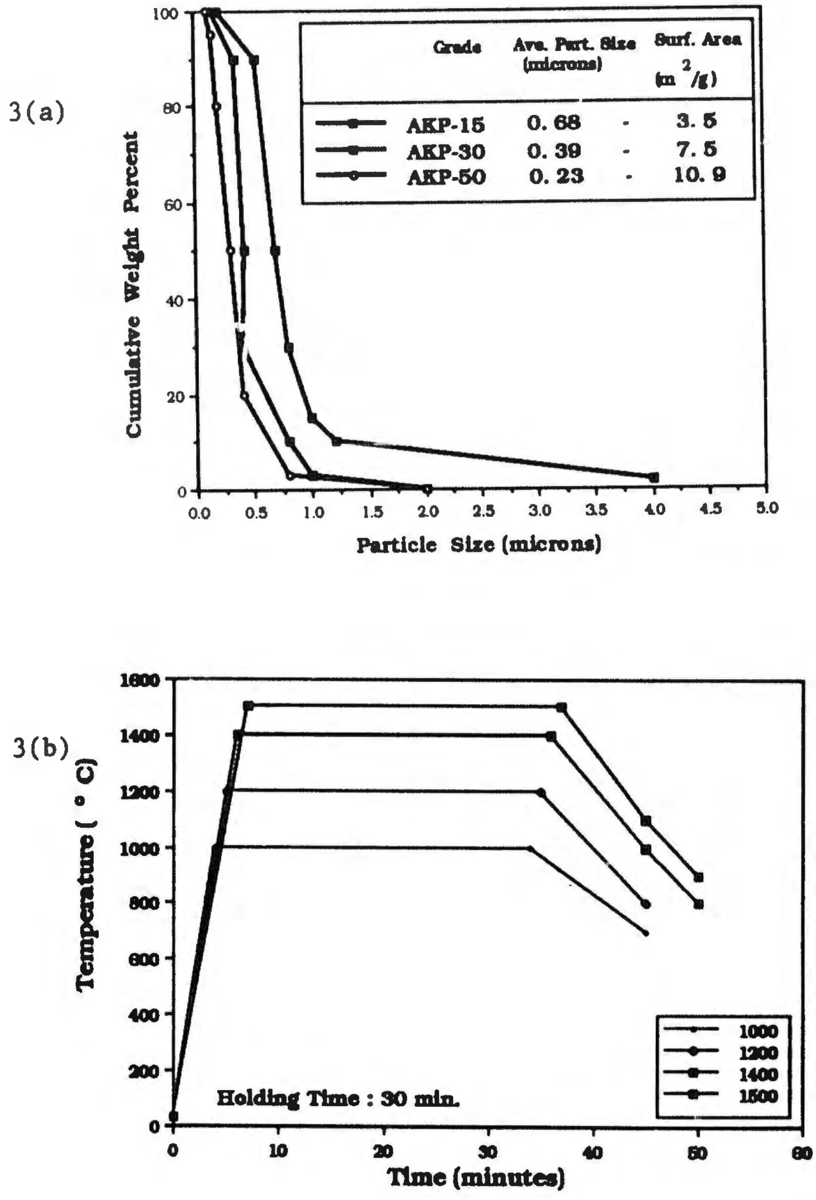
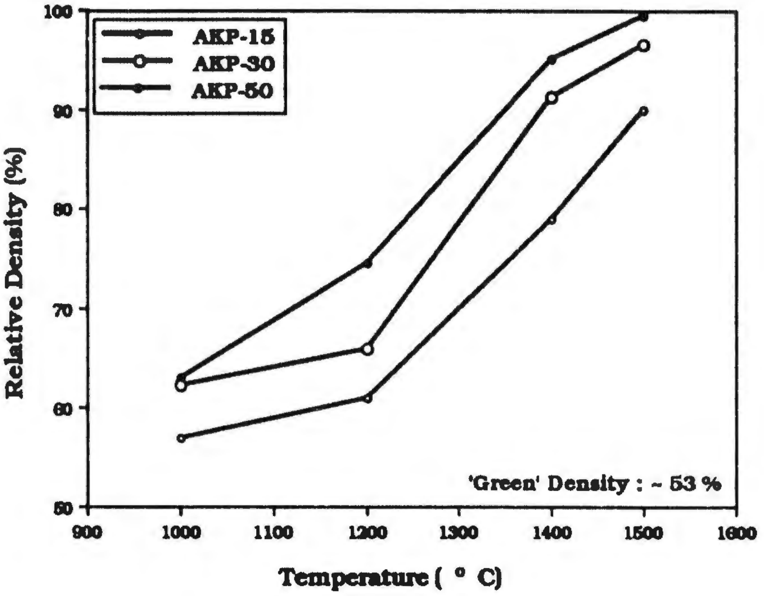


Figure 3. Effect of particle size on the MW (hybrid) heating of AKP alumina::
(a) Particle Size Distribution of AKP alumina (as-received)
(b) Temperature-Time Sintering Cycles (holding time -30 minutes)

3(c)



3(d)

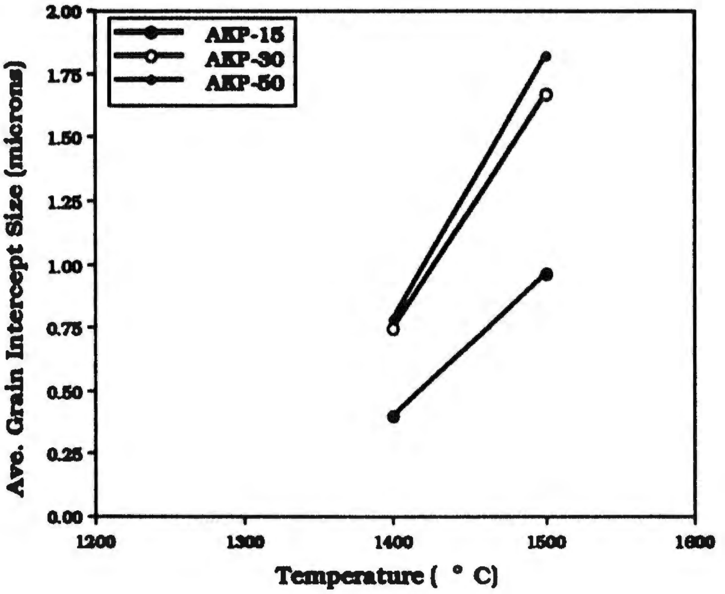


Figure 3. Effect of particle size on the MW (hybrid) heating of AKP alumina:
(c) Relative Density vs. Temperature (d)
(d) Grain Intercept (GI) Size vs. Temperature

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