Alumina Based Ceramics: Microwave Fabrication and Properties Development

Tarun Bhatnagar[1] Rahul Lodha[2]
[1]PG Scholar [2]Deputy Director
[1]Department of Chemical Engineering
[1,2]Mewar University, Chittorgarh, Rajasthan, India

Abstract— The enhancement of sintering rates and other solid state reactions during microwave heating on a variety of ceramics have been reported in literatures. These empirical observations of microwave enhancement have been broadly called the “microwave effect”. However, there has been little published work which directly compares the compositional dependence and green sample fabrication on the properties developed by microwave effect on alumina ceramics. Therefore, this research proposal designs to conduct a series of experimental to investigate the effects of the compositional dependence and green sample fabrication on the properties developed by microwave effect on alumina ceramics by using 2.45 GHz microwave power. And to study the effects of green samples, biaxial pressed alumina samples are to be prepared by pressing at different pressures. It is known that the mechanisms responsible for the decrement in sintering may attribute to decrease in microwave effect or different the transport path, such as volume diffusion mechanism, instead of mainly grain boundary diffusion, which is usually reported in microwave sintering. This leads to requirement for further development such that microwaves preferred heating grain boundary areas are directed to heating within the grains.

Key words: Flakes graphite, Alumina Metal Powder (-150 µm), Boron Carbide Powder, Alumina A16

I. INTRODUCTION

Microwave sintering of ceramics can be advantageous over sintering using conventional furnaces, with the possibility of rapid heating. This is because the ceramic is heated directly by microwave power, which depends on its loss tangent and the amount of incident microwave power incident. Due to rapid heating, the non-isothermal processes such as segregation of impurities to grain boundaries can be minimized and abnormal grain growth can also be reduced. Minimizing both abnormal grain growth and non-isothermal processes have the general advantage of improved mechanical properties of the ceramics. The possibility to achieve uniform heating is based on the property of most ceramics, having low loss tangent in microwave frequency ranges at ambient temperatures. This contrasts to conventional heating in which a non-uniform heating is easily occurred.

Microwave with 2.45 GHz frequency is being the most commonly used because of its availability and feasibility. Even for ceramic processing, 2.45 GHz systems with KW range of power are widely available. The wavelength of 2.45 GHz microwave is 12.2 cm, which is similar to the dimension of the commonly used applicators. In order to reduce the effect of the hot spots because of similarity of size, the option to change the size of the applicator or the microwave frequency should be a possibility. Using the microwave technology for alumina can be a valuable addition for use in the known fields of applications of alumina ceramics as for ballistic armour, electronic substrates, element former, thread guides, high voltage insulators, laser cavities, radomes, wear components like blades, valves and guides.

Sintering using a higher microwave frequency not only opens the possibilities for more homogeneous processing but also may get a higher “microwave effect”. Besides, a new special effect may be observed which open possibility to process material by using low cost and better properties. Moreover recent experimental evidence supports the fact that microwave effect leads to an enhancement of the sintering processes taking place in various ceramics; microwave frequencies up to the millimeter wave (MMW) range, were more published. However, despite the potential implication of microwave processing for the ceramic industry, there has been little published work which directly compares the microwave frequency effects on ceramic sintering.

II. RESEARCH METHODOLOGY & EXPERIMENTAL WORK

A. *Raw Materials*

Commercially available natural flakes graphite, aluminium metal powder (- 150 µm), boron carbide powder and alumina will be used to maintain the granulometry of the mixture. In this present work, high purity alumina is taken as the raw material considering the Selection criteria like purity, low Fe_2O_3 content and crystals in the range of 5-1500 µm.

Impurities	SiO2 (0.07%), MgO (0 %), Na_2O (0.07%), Fe_2O_3, CaO, B_2O_3
Structure	Hexagonal (rhombohedral)
Theoretical density	3.97 g/cm^3

Table 1: Properties of alumina A16

B. *Preparation of Powder*

In order to distribute the mix homogeneously, 15 min milling in a steel container rotating at a speed of 400 r.p.m. with silicon nitride balls as the abrasive media will be carried out. The mixing ratio of alumina to liquid media was 0.70:1.The aged mixtures will be pressed uniaxial by hydraulic press in a steel mould. An appropriate weight of each mixture will be taken to get the desired green density and the size. The powder was dispersed in de-ionized water with 0.3wt% dispersant, an ammonium polycarboxylate acid. The dispersant was added to the slurry to prevent the agglomeration of the suspended alumina particles. To remove hard agglomerates, prior to compaction, the powders were ball milled in an alumina jar for a day. A cylindrical sample with a diameter of 15 mm, and a height of 5 mm was formed by slip casting. Because estimation of penetration depth of 2.45 GHz waves is about 8 mm at room temperature, this sample size was expected to provide enough penetration depth.

To investigate the effect of green samples, this work adopted cold isostatic pressing (CIP) method. Cold isostatic pressing involves the application of hydrostatic pressure to a rubber mold containing samples. The CIP's pressure results in force equally along all directions of the samples. A schematic of this situation is shown in Figure 1. The CIP was performed before drying because it would result in a higher density of green samples. To optimize the CIP treatment for green samples, firstly the samples were pressed by varying the pressure and then followed by varying the holding time for each pressure.

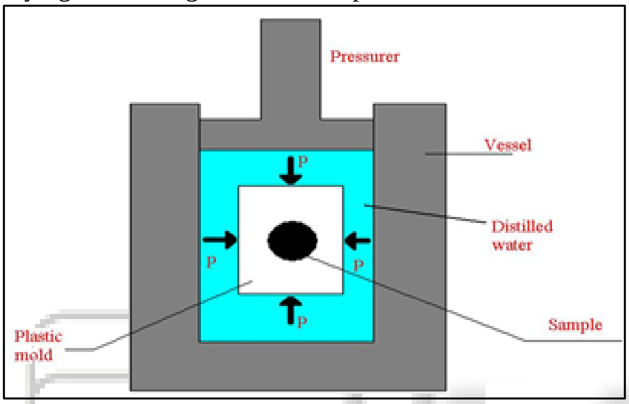

Fig. 1: Schematic of Cold Isostatic Pressing

C. *Drying and Pre-Sintering*

After slip casting, the samples were air dried at 110°C for 2 hours and then pre-sintered by heating in an electric furnace for 2 hours at 700°C to remove all water, deflocculants and any organics that may have been introduced during processing. Based on the sample density measurement before and after pre-sintering, the relative sample density increased by 1-3 % of the TD. The samples after pre-sintering are green samples. The average relative density of the green samples was approximately 55.5 % of TD. After the pre-sintering, samples were then sintered by using two sintering methods, microwave (2.45 GHz), and conventional (Electric Furnace). The detail of sintering setup is explained in the following sections.

D. *Microwave Treatment*

Using water and other additives, a mode of design based on trial and activation energies will be developed to achieve the right composition for 2.45 GHz absorption and heat transfer coefficients that will be calibrated vs. available sintering mechanisms. The microwave had a frequency of 2.45 GHz with rating to operating temperature of 1050°C.

III. RESULTS & DISCUSSION

A. *Green Sample*

The samples after pre-sintering were referred as green samples. Because sintering depends on the green sample properties, the properties such as density and microstructures of samples were well characterized before sintering. The average relative density of the green samples was 55.5 % of theoretical density (TD). Pressure at 150 MPa, the green sample density averagely increased 2.8 %, from 55.5 % to 58.3 %.

No	Sample	Relative density (%)	Grain size (m)
1	Pressed Uniaxially	55.5	0.35
2	Cold Isostatic Pressed	58.3	0.35

Table 2: Properties of the green samples

B. *Investigation Effect of Microwave Frequency*

To study the microwave frequency dependence of the "microwave effect" on the properties of the sintered alumina, sintering a high purity alumina at 2.45 GHz as well as by conventional heating.

C. *Verification of Volumetric Heating In MW Sintering*

To investigate the microwave effect, enough penetration of microwaves throughout the samples or a volumetric heating must be achieved. Because loss tangent of alumina in SMMW range is much higher than that at other lower frequencies, a surface heating easier occurs than other lower frequencies. Thus, a careful volumetric heating examination at this microwave frequency was performed.

Figure 2 shows a photograph of a successfully MW sintered alumina sample at a sintering temperature of 1500°C. It shows that a significant shrinkage, without cracking, was achieved. To evaluate the effect of microwave, enough penetration of waves throughout the samples or a volumetric heating must be achieved.

Fig. 2: Photograph of alumina (a) green compact and (b) MW-sintered sample at 1500 ºC.

Generally, the microwave effect on the densification and grain growth found in this study, and as reported by several researchers as well, indicated that microwaves enhanced the (mass transport flux) during sintering. Thus, the decrement in densification observed in MW sintered alumina could also be attributed to that a lowered microwave effect could lead to a decrease in mass transport rate or to the alteration of transport mechanism during sintering. An experiment to estimate the driving force is not easy to perform because the force is dependent on not only the density and grain size but also the electric field in the materials.

D. *Results of Apparent Activation Energy (Q) Estimation*

Figure 3 is a densification curve of unCIPed alumina in MMW and conventionally with different holding time. It depicts that the sintering rates were determined at the same densities. For the unCIPed samples, sintering rate at 80% and 70% of TD were determined and plotted against the reciprocal of absolute temperature in a standard Arrhenius plot. Since the densities lay in the intermediate stage of sintering where no significant grain growth occurred so that effect of grain size and density variations can be minimized. The sintering rate at 80 % of theoretical density against the reciprocal of the absolute temperature in a standard Arrhenius plot for the unCIPed samples shows the apparent activation energies for sintering the unCIPed samples. The apparent activation energy in conventional sintering was 522±27 kJ/mol, whereas that in MW sintering was only 427±30 kJ/mol. The apparent activation energy in conventional sintering in this study was in agreement with that for oxygen lattice diffusion in alumina. Estimation of apparent activation energy in MW sintering was performed based on the Young and Coutler’s method. The method has also been used for estimating apparent activation energy by several researchers.

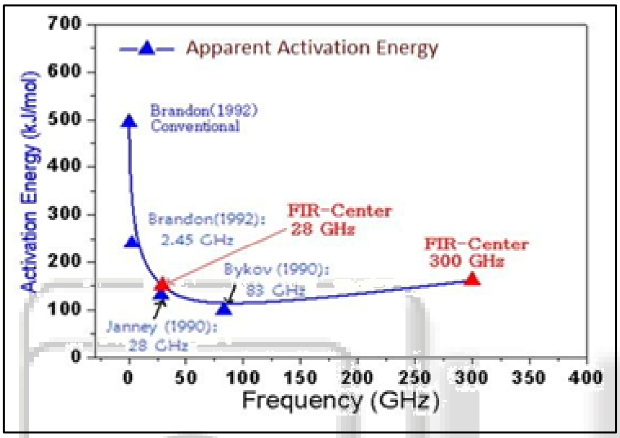

Fig. 3: Dependences of apparent activation energy of alumina with microwave frequency

The result of apparent activation energy in SMMW was higher than that in MMW suggested that diffusion in SMMW sintering was slower which led to the lower densification. However, both SMMW and MMW`s apparent activation energy values were much lower than those from conventional sintering. There are several efforts have been done for explaining the enhancement. Yet, there are no satisfied theories for the phenomena. Some people believe that the electric field is preferentially heated the grain boundary resulting in the enhancement of the grain boundary diffusion during sintering. This enhancement was then observed as a decrease in apparent activation energies. Recent theory developed by Rybakov and Semenov proposed that microwave induced a new additional driving force known as ponderomotive force (PMF) which inducing diffusion of ionic crystalline materials. However, characteristic magnitude of PMF is not large. The measure of the corresponding stresses is the radiation pressure of electromagnetic wave under which the condition of most microwave processing experiments does not exceed 0.1 Pa.

Another possibility effect of MW is altering pre-exponential factor, D0. The pre-exponential represents the number of atomic jump per time. It is dependent on the jump frequency (ν) of the atoms as well as the inter-atomic distance (λ) at the reaction interface, $D_0 = \gamma\nu\lambda^2$. Of these, it might be reasonable assumed that geometric factor γ and λ□ will not affected by presence of microwaves, because it determined by crystal structure of material. Thus the jump frequency (ν) is the only one possibility for being affected by microwaves. However, there is insufficient clear evidence to draw conclusions in this work for the phenomena.

E. Effect of Microwave Frequency on Grain Growth

The densification, as well as the grain growth, is a result of atom diffusion in material. During sintering, a mixture of the diffusion mechanisms must occur, but they shift in dominance, depending on the sintering conditions. This suggests that the densification rate is not only affected to densification but also closely related to the microstructure of material. The investigation and comparison of grain growth can lead to a better understanding of effect of microwave frequency.

Because the grain size strongly depends on the density of sintered samples, the grain size comparison among different methods was obtained at the same density. Figure shows the plot of the grain size with an increasing sample density. The variation of the particle sizes with density was not significantly different among the annealing methods up to a density of approximately 85 %. Over 85 %, however, all methods showed a rapid grain growth with the biggest grains were observed in the conventional methods.

Sintering Temperature	Time consumption (minutes)	
	Conventional	MW
1000	200	27
1500	300	43
1700	380	52

Table 3: Comparison of time consumption for SMMW and conventional methods

The difference in grain sizes between electromagnetic wave heating (SMMW and MW) with that the conventional was due to the difference in sintering time. Time consumption in conventional heating was much longer than that in SMMW and MW. To achieve a sintering temperature of 1500 ºC, for example, MW processing needed 43 minutes, while the conventional method needed 300 minutes, as shown in Table 3.

A similar phenomenon was reported by Coble for producing transparent alumina by using MgO, in which an enhanced densification rate relative to the rate of normal grain growth was observed. His research led to the conclusion that MgO did not inhibit grain growth but it increased the sintering rate such that discontinuous grain growth did not have time to form. As a result of fast heating in MW, it also appeared in this study that the grain growth did not have time to form. However, at high sintering temperatures up to 1400ºC, the grain sizes in both methods were found almost the same. It is because at early stage of sintering, pores inhibited the grain boundary movement. When a number of pores (and other inclusions) are decreased (or the sample already has a high density), grain growth will easily occur.

F. Effect of Green Sample on the Properties of Sintered Alumina

Microwave effect is dependent on many parameters such as microwave frequency, green sample`s properties, atmosphere, and microwave energy. To study green samples’ dependence on the `microwave effect`, two green samples, cold isostatic pressed (CIPed) and uncold isostatic pressing (unCIPed), were prepared.

The mechanisms by which the CIP enhances the densification in MW sintering are not fully understood yet. However, a difference in the TD of green compact before sintering is surely the reason. These two resulted in an increase in the number of grain boundaries per unit volume which in turn led increase coupling of microwave radiation to samples. As the result, the rate of mass transport is also increased.

As in unCIPed samples, the change in densification as shown in Figure 4 also corresponds to the rate, which could be attributed to alteration in microwave effect which led to alteration in mass transport rate or the transport mechanism during sintering which could be associated with a decrease in driving force or in apparent activation energy. Thus, a series of experiments for estimating the apparent activation energy on CIPed samples was performed.

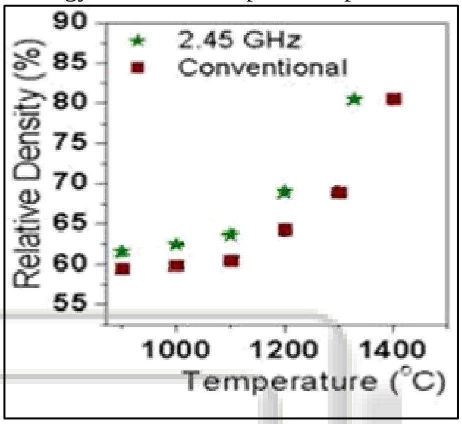

Fig. 4: Relative density for CIPed samples sintered by conventional method

As in unCIPed samples, the change in densification rate could be attributed to alteration in microwave effect which led to alteration in mass transport rate or the transport mechanism during sintering which could be associated with a decrease in driving force or in apparent activation energy. Thus, a series of experiments for estimating the apparent activation energy on CIPed samples was performed, as shown in Figure 5.

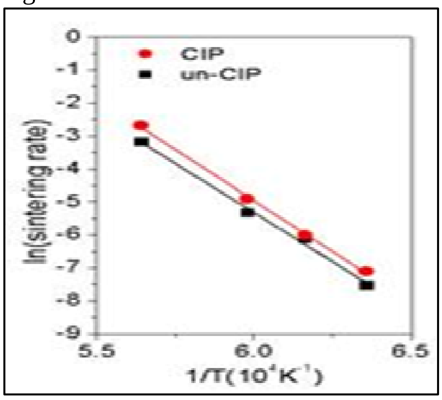

Fig. 5: Arrhenius plot for activation energy by conventional method

A decrease in the apparent activation energy of approximately 12 % was observed in MW sintering, compared to that of only 4 % observed in conventional method. The mechanisms by which the CIP enhances the densification decreased apparent activation energy on CIPed samples likely as a result of different green compact microstructures before sintering. The increase in number of grain boundaries per unit volume resulted in enhanced the coupling of microwave radiation to CIPed samples. This result suggests that microwaves prefer to heat grain boundaries than grains. The illustration of the mechanism is described in Figure 6.

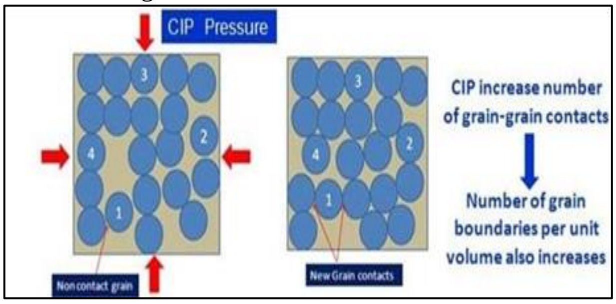

Fig. 6: Possible mechanism for CIP increase densification of sintered alumina

G. Hardness Improvement Related To Microwave Enhanced Sintering

Alumina is extensively used as an engineering ceramic due to its superior mechanical properties. However, its mechanical properties depend on its density as well as its grain size. Generally, for ceramics with grain size bigger than 10 nm, the finer its grain, the higher its strength (Hall-Petch relation). This section presents the experimental results of mechanical properties (hardness and fracture toughness) of sintered alumina samples. Higher hardness on MW sintered samples than that on conventional ones was observed because, at the same density, the SMWW sintered samples had finer grain sizes. However, at the same sintering temperature, samples of the two methods have different densities. Table 4 shows the hardness of the two sintering methods at approximately the same density.

Sintering Method	(%)	(µm)	(kgf/mm^2)	
Conventional	96.2	1.05	1284	
MW	96.0	0.76	1918	

Table 4: Micro hardness of un-CIP alumina for different sintering methods

It was found that MW samples had a significantly higher hardness. This result is in good agreement with Hall-Petch's relation on the grain size range. From the application's point of view, this result is interesting because it indicates the possibility to produce an alumina compact which has not only a higher density but also a higher hardness through rapid sintering using MW as depicted by the values of hardness in Table 5

Sintering Method	Rel. Density (%)	Grain Size (µm)	Fracture Toughness (MPa/m$^{1/2}$)
T = 1500°C			
Conventional	82	0.37	1.07
MW	87	0.43	1.02
T = 1600°C			
Conventional	96	1.06	1.79
MW	95	0.82	2.68
T = 1700°C			
Conventional	98	2.37	0.74
MW	98	1.12	0.58

Table 5: Fracture toughness of un-CIP alumina at different sintering temperature

The grain size has likely played a key role on the alumina hardness. In the case of CIPed samples, the grain sizes of the samples processed in MW is finer and, thus, had a higher strength, than those processed in conventional method. Table 6 shows the hardness from the two sintering methods at the same density. The bigger differences in grain sizes led to that MW had a much higher strength.

Sintering Method	Rel. Density (%)	Grain Size (µm)	Micro-Hardness (kgf/mm^2)
Conventional	97.2	2.62	1280
MW	97.2	0.58	2190

Table 6: Micro hardness of un-CIP alumina for different sintering method

IV. Conclusions

A study on microwave effect on alumina properties was performed. Generally, the microwave effect depends on many parameters such as microwave frequency, green sample`s properties, atmosphere, and microwave energy. In this study, microwave frequency and green sample’s dependence of ‘microwave effect’ to the properties of sintered alumina was carried out.Two main alumina properties for closely related applications were density and hardness. Firstly, the effects of microwave frequencies on densification were evaluated. Experiment results revealed that the densification of microwave heating was higher than that of conventional sintering, as well. The mechanical properties of MW sintered alumina were tested by using micro Vickers’ hardness testing. However, a further analysis to understand the mechanism by which MW on densification and hardness must be carried out.The decrease in densification observed in SMMW sintered alumina could be attributed to a lowered microwave effect that led to a decrease in mass transport rate or an altered transport mechanism during sintering. This could be associated to the decrease in either driving force or apparent activation energy of diffusion. An experiment to estimate driving force is not easy to perform because the force is dependent on not only the density and grain size but also the on electric field in the materials.

It is believed that the electric field is preferentially heated the grain boundary resulting in the enhancement of the grain boundary diffusion during sintering. This enhancement was then observed as a decrease in apparent activation energies, but that is a subject for further investigation. Another phenomenon in sintering is grain growth. Grain growth is also diffusion-controlled process in solid state sintering of alumina. Thus, microwave effect can be also attributed to altering in mass transport rate parameters or altering the transport mechanism during sintering as in densification phenomena.

The higher hardness of MW samples found in this study was probably due to the smaller grains of the samples (Hall-Petch relationship). Furthermore, it was also found that MW sintered alumina had a higher fracture toughness at most sintering temperatures. However, mechanisms for the hardened alumina in this study are not clear. The evaluation on the effects of green compact on densification demonstrated that cold isostatic pressing (CIP) treatment significantly increased densification in MW. The examination on the effects of green samples in SMMW sintering demonstrated that the CIP treatment on alumina before sintering effectively not only accelerated sintering but also suppressed the grain growth.

References

[1] Dé, I. Ahmad, E. D. Whitney and D. E. Clark, Effect of Green Microstructure and Processing Variables on the Microwave Sintering of Alumina, Mater. Res. Soc. Proc. 189, pp. 283-288 (1990).
[2] Goldstein, N. Travitzky, A. Singurindy, and M. Kravchik, Direct Microwave Sintering of Yttria-stabilized Zirconia at 2.45GHz, J. European Ceramic Society 19, pp. 2067– 2072(1999).
[3] A.C. Metaxas and R. J. Meredith, Industrial Microwave Heating, Peter Peregrinus, London, (1988).
[4] Hallstedt,ThermodynamicAssessmentof the System MgO–Al2O3,J.Am.Ceram.Soc.,75[6],p.1502 (1992).
[5] E. Holcombe and N. L. Dykes, Microwave Sintering of Titanium Diboride, J. Material Science, 26[14], p.3730 (1991).
[6] Cozi, Z. Fathi, and D. E Clark, Crystallization of Sol Gel Derived Barium Aluminosilicate in a 2.45 GHz Microwave Field, Microwave: Theory and Application in Material Processing II, Cer. Trans. 36, Am. Cer. Soc., Ed. By D.E Clark, W. R. Tinga, and R. Laia, p. 317 (1993).
[7] W.D. Kingery, H. K. Bowen, D. R. Uhlmann, Introduction to Ceramics, John Wiley, NewYork (1976).
[8] W.H. Gitzen, Alumina as a Ceramic Material, Am.Cer. Soc., Columbus, USA (1970)
[9] Boonyapiwat and D. E. Clark, Nucleation and Crystal Growth of Li2O-2SiO2 in Microwave Field, Microwave: Theory and Application in Material Processing III, Cer. Trans. 59, Am. Cer. Soc., Ed. by D.E Clark, D. C. Folz, S. J. Oda, and R. Silberglitt, p. 505 (1995).
[10] Dé, I. Ahmad, E. D. Whitney and D. E. Clark, Effect of Green Microstructure and Processing Variables on the Microwave Sintering of Alumina, Microwave Processing of Materials II, pp. 283-288(1990).