Millimeter-Wave Technology for Powder Processing

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Abstract

Microwaves face growing industrial interest as a materials processing technology. They allow instantaneous volumetric heating of dielectric materials leading to a reduction of process time and therefore energy consumption in comparison to conventional heating where energy is deposited to the materials surface and transferred to the volume by thermal conduction. This benefit is most distinctive for materials with low thermal conductivity such as, polymers, glasses, powders of powder compacts. The following paper demonstrates the benefits of microwave technology for processing of high purity alumina powder. The phase transformation of γ-Al_2O_3 into the chemically and thermally more stable α-Al_2O_3, which is used in ceramic industry, has been enhanced.

1 Introduction

Within the last decades there has been growing interest from industry in microwave technology for materials processing. Various process technologies using microwaves have successfully been implemented in several industrial fields, such as drying, food processing or polymer curing and vulcanisation and many others. The use of microwave technology in a thermal process may be beneficial for all types of dielectric materials with low thermal conductivity. During a conventional heating process heat is deposited by IR radiation or convection in the materials surface only. Heat is transfered into the volume by thermal conduction. This can be very time consuming especially with large volume products of low thermal conductivity such as polymers, powders, powder compacts, glasses and others. Microwave energy can be directly transferred into the materials volume wh+ere it is converted into heat by different absorption mechanisms such as electronic or ionic conduction or dipole relaxation processes. Therefore an instantaneous volumetric heating can be realized. For specific materials which show low dielectric loss or require homogeneous heating the application of frequencies higher than the wide spread industrial frequency of 2.45 GHz is beneficial, since power absorption is increasing with frequency and the realization of a homogenous field distribution is much easier.
The benefits of a compact gyrotron processing system operating in the millimetre-wave (mm-wave) range at 30 GHz have been demonstrated on a high temperature process employed for the production of high purity α-Al_2O_3 powder used in ceramic industry. One of the conventional routes for the production of alumina ceramic powders uses a two-step thermal process in gas fired furnaces. In a first step thermal decomposition of alum leads to γ-Al_2O_3 and in a second step phase transformation into α-Al_2O_3 has to be performed. Since powder materials have extremely low thermal conductivity, the conventional process suffers from strong thermal gradients during the heating cycle. Therefore the conventional process is time consuming. Here the mm-wave inherent volumetric heating could be an essential advantage for the process, since asignificant reduction of the processing time can be realized.

2 Experimental Set-up

2.1 Gyrotron System

In 1994 at the Forschungszentrum Karlsruhe a compact prototype gyrotron-system was installed for materials processing. It includes a 30 GHz gyrotron from the Institute of Applied Physics, Nizhny Novgorod, Russia which allows continuous wave operation at the second harmonic of the electron cyclotron frequency in the TE_{02} cavity mode with an efficiency of about 30 % (U_b=23 kV, I_b=2 A) [1]. The mm-wave output power of up to 15 kW is coupled into an applicator of about 100 l volume via an improved quasi-optical transmission line. The heating process is fully computer controlled in that way, that the temperature measured with a thermocouple, placed in the volume of the powder sample, is following any preset temperature-time program. A calibration of the thermocouples by measuring the melting point of gold yields an error of less than 1%

2.2 Hybrid Heating Module

Applying conventional heating the sample surface is hotter than the sample volume. Microwave volumetric heating typically results in temperature gradients the other way round if the hot sample faces cold oven walls. To reduce convection and radiation losses from the sample surface during microwave heating, an adequate thermal insulation typically made from alumina or mullite ceramic fibre boards has to be arranged around the sample. Eliminating this inverse temperature profile can be performed by raising the temperature of the inner wall of the thermal insulation to the level of the centre temperature of the sample. This can be realized by conventional resistive heating. The combination with microwave heating, so called hybrid heating allows an active control of the temperature profile within a powder batch.

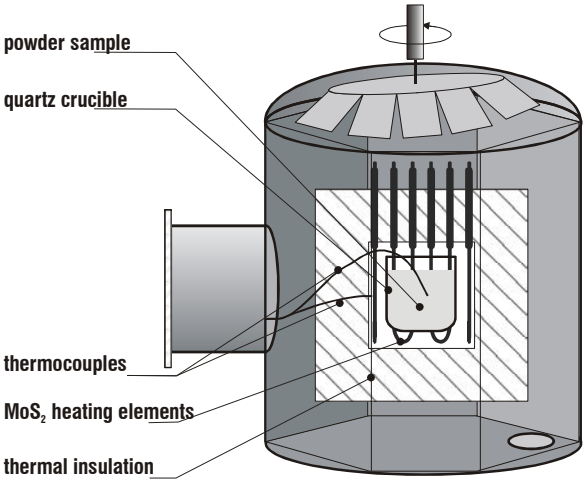

Fig. 1: Schematic drawing of the hybrid heating setup.

Such a hybrid heating module has been developed and installed in the mm-wave applicator [2]. It consists of a box made from mullite ceramic fibre boards (inner dimensions: 130 x 130 x 130 mm^3; fiber board thickness: 60 mm) including eight 300 Watts $MoSi_2$ heating elements, distributed along the side walls (see Fig. 1 and 2). This is a small design with a usable volume of 1 litre only, but it allows the insertion into the existing mm-wave applicator without large constructive changes. The maximum working temperature of this oven is 1650 °C. It can be operated with various gas atmospheres. This equipment has the unique possibility to investigate the influence of different heating methods on the material performance in a single system. That means identical temperature sensors are used for mm-wave heating, conventional heating and hybrid heating so that systematic errors in temperature measurement can be excluded.
A negative effect of such a hybrid heating technology might be that mm-wave power has to be switched off as soon as the final temperature in the sample volume has been reached. Then only conventional heating is needed for compensation of radiation and convection losses from the sample surface. This means that any mm-wave specific effects to the processes such as enhancement of diffusion can only be expected to be present during the heating cycle.

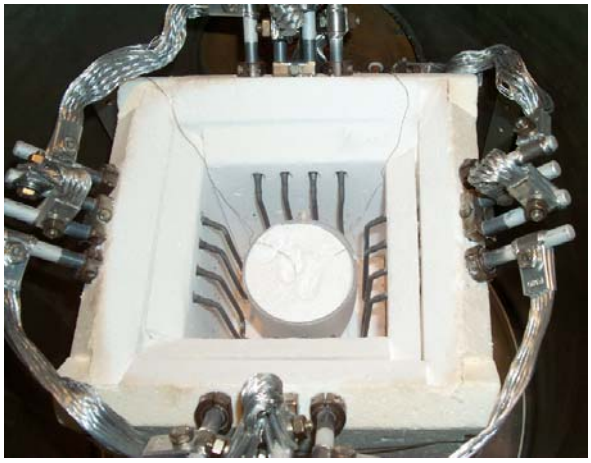

Fig. 2: Photograph of the hybrid heating module including a powder batch.

2.3 Powder Material

The aim of this work was to produce a high purity α-alumina powder with a crystallite and particle size as small as possible to be used as raw material for high quality alumina ceramics with improved materials properties. The industrial route for α-alumina powder production is a two-step thermal process starting with alum as raw material [3]. Within the first process step γ-alumina is formed by thermal decomposition of alum. To get the chemically and thermally stable α-alumina phase a second calcinations process has to be performed at temperatures of about 1150 °C. But this phase transformation process is always accompanied by grain growth since it needs high temperatures and long processing time.
This second process step was investigated. The γ-alumina powder used as starting material has a purity of 99.99% and a BET specific surface of about 95 m^2/g which corresponds to an average particle size of 16 nm. This extremely fine grained powder results in a XRD graph showing only weak and broad peaks hardly distinguishable from the noise level (see black straight line in Fig. 4). The powder was processed in a crucible made from high purity quartz (see Fig. 2). The outstanding feature of this crucible material is the temperature stability and high microwave transparency.

2.4 Materials Characterization

The processed powder samples were characterized by BET and XRD method to optimise the process pa-

rameters. BET measurements give information about the specific surface area s and allows, assuming spherical particles, to estimate an average particle size D from the following relation [4]

$$D = \frac{6}{\rho s} \qquad (1)$$

where ρ is the materials density.
XRD measurements allow to analyse the phase composition of the processed powder samples comparing the peak area of the α-alumina peak with the areas of equivalent peaks of a fully transformed alumina powder. Additionally from the full width half maximum of the XRD peaks the crystallite size d can be estimated according to the Debye-Scherrer formula [5]

$$d = \frac{K\lambda}{L^* \cos\theta} \qquad (2)$$

where L^* is the full width half maximums of the diffraction peak corrected for the instrumental peak broadening. The x-ray wavelength λ was 1.542 Å which corresponds to the Cu $K_{\alpha 1}$ line. K is a geometrical factor and θ is the diffraction angle.

3 Experimental Result

3.1 Temperature Distribution in Powder Batch

The mm-wave assisted resistance heated furnace described before was used for processing of γ-Al_2O_3 powder samples with varying process parameters such as calcinations temperature and isothermal dwelling time. The maximum volume size which was processed in this lab-scale installation is about 300 cm^3. The temperature distribution in such a powder batch has been investigated for the different heating regimes: pure conventional, pure mm-wave and mm-wave assisted or so called hybrid heating. The graphs in Figure 3 show the temperature measured at the wall (open symbols) and in the sample volume (closed symbols) (Fig. 3 top) and the resulting temperature gradients T_{sample}-T_{wall} (Fig. 3 bottom) for a heating cycle up to 1250 °C with a heating rate of 20 °C/min and one hour dwelling time. It can be clearly seen that only by using a combination of conventional and mm-wave heating, the temperature gradients can be controlled to almost zero. At any other case the temperature gradients can be as big as 300 °C, even within such a small powder batch, but with different sign if one compares pure conventional and pure mm-wave heating. While with volumetric mm-wave heating the temperature in the centre volume is higher than the temperature at the wall, the volume temperature for conventional heating is far below the temperature of the oven wall but converges to the volume temperature during isothermal dwelling. The small temperature peak at the initial phase of isothermal dwelling indicates the exothermal phase transformation process from γ-alumina to α-alumina accompanied by additional volumetric heating.

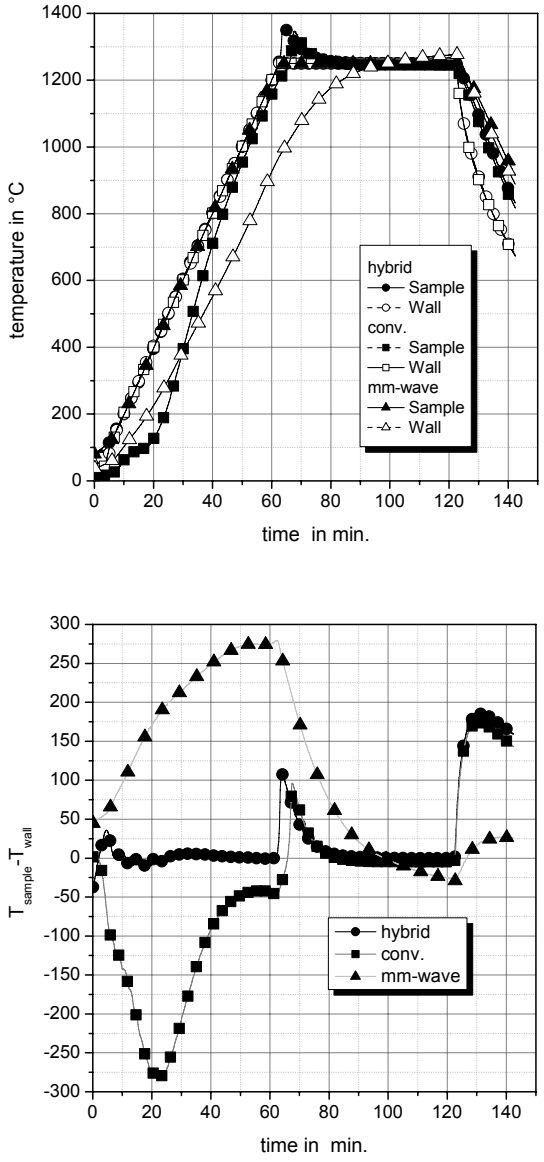

Fig. 3: March of Temperature (top) and temperature gradients (bottom) in a 300 ml powder batch for different heating methods.

3.2 Phase Transformation

For investigations of phase transformation a series of experiments has been performed with a dwelling time of one hour in a temperature range from 1100 °C to 1250 °C by conventional and hybrid heating in the

above described set-up. XRD results clearly show stronger α-alumina peaks in case of hybrid heating in comparison to the conventional process (see Fig. 4). This demonstrates an enhanced phase transformation with hybrid heating.

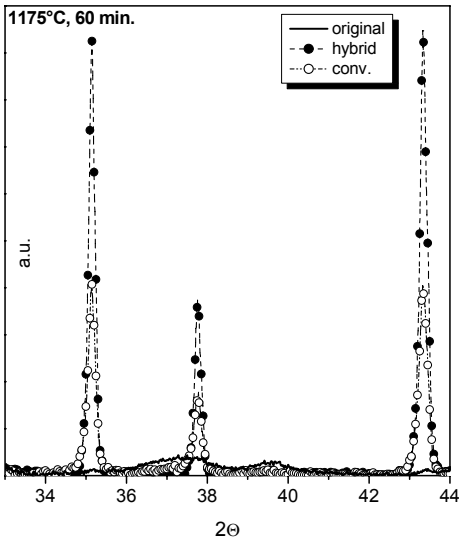

Fig. 4: XRD results for powders processed by conventional and hybrid heating at 1750°C for 60 minutes.

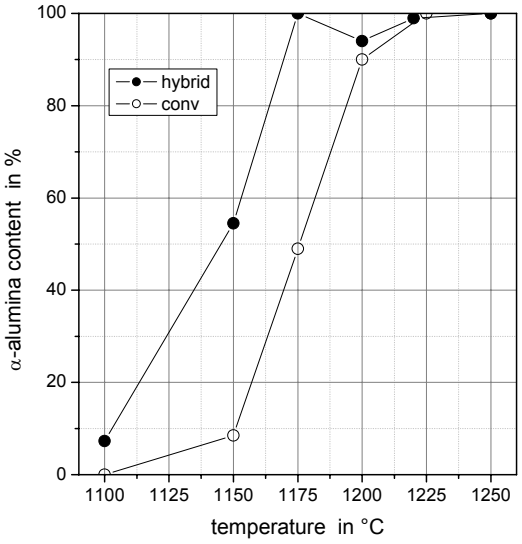

Fig. 5: α-alumina concentration as a function of temperature for hybrid and conventional processing.

The α-alumina concentration was estimated from the area of the XRD diffraction peaks of the processed powder samples and plotted in Figure 5 as a function of temperature. In contrast to conventional heating with hybrid heating the phase transformation process occurs at temperatures which are about 50 °C lower. There are two possible explanations for this effect. As shown in chapter 3.1 with hybrid heating the temperature profile is much more homogeneous than with conventional heating, leading to a more homogeneous and therefore more rapid transformation process. But an additional effect might be the enhancement of diffusion processes during phase transformation under the influence of electromagnetic fields. This has been described as an effect of ponderomotive forces in ionic materials enhancing solid state sintering as well [6]. The microwave specific absorption in the previously described powder process is assumed to be dominated by relaxation of lattice defects within the applied alternating electric field.

3.3 Grain Size

The phase transformation which is a diffusion controlled process is always going along with a growth of crystallite size and an aggregation to larger particles. Both effects should be suppressed as much as possible. While crystallite size was estimated from XRD results, information about particle and aggregate size could be taken from the specific surface of the powder samples measured by BET method. The larger the surface the smaller the particle size.

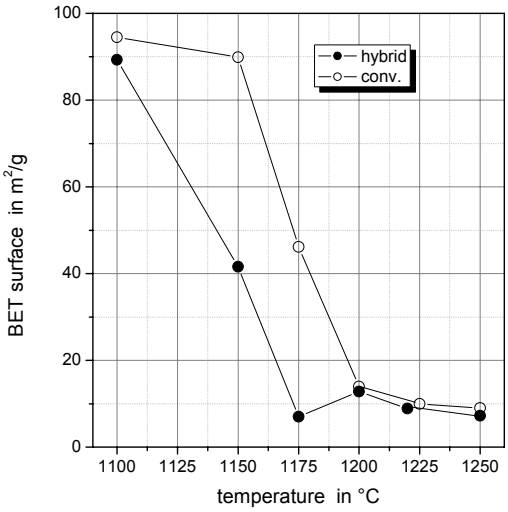

Fig. 6: BET specific surface area as a function of temperature for hybrid and conventional processing.

The specific surface of the original powder of about 95 m^2/g decreases to less than 10 m^2/g which corresponds to an average particle size of more than 150 nm. The specific surface during hybrid heating decreases at lower temperatures than during conventional heating. This is consistent with the enhanced phase transformation under the influence of microwaves derived from Fig 5. If the specific surface is plotted as a function of the α-alumina content as shown in Fig. 7, hybrid and conventional processing

are not distinguishable. No influence of microwaves on the aggregate size can be observed considering BET measurments. Comparing the evolution of the α-alumina crystallite size during phase transformation (see Fig. 8) by evaluation of XRD measurements according to equation (2) powder with slightly smaller crystallites can be obtained under the influence of microwave radiation. If phase transformation is completed the ongoing annealing process promotes further grain growth which should be avoided. One hour dwelling at an optimised process temperature results in an average grain size after full phase transformation of about 70 nm in comparison to 80 nm achieved by conventional heating.

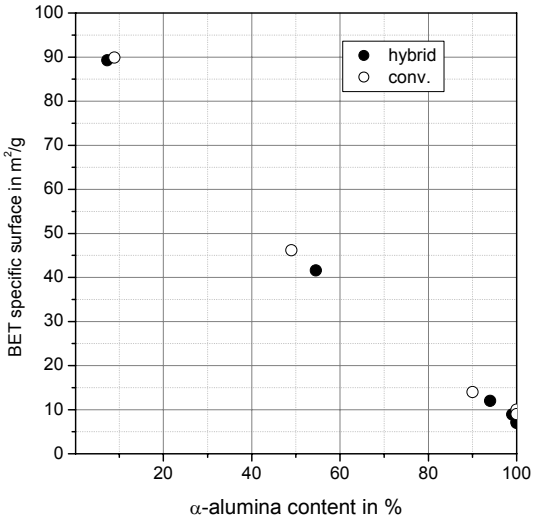

Fig. 7: Evolution of BET surface with phase transformation during different heating methods.

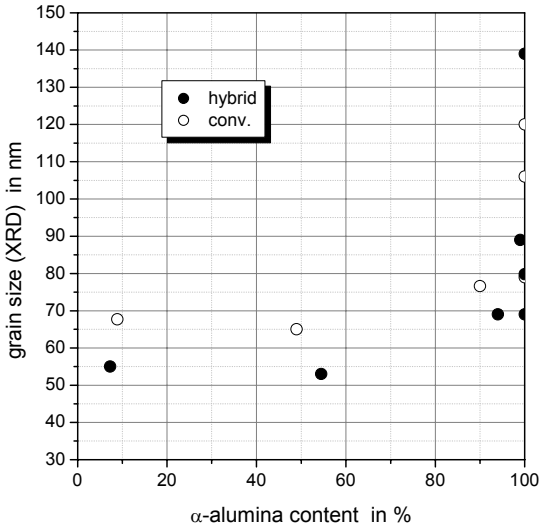

Fig. 8: Grain growth during phase transformation for different heating methods.

4 Summary and Conclusions

Detailed investigations have been performed on the phase transformation of high purity γ-alumina to α-alumina under various heating conditions. While conventional as well as pure microwave heating suffer from temperature gradients within a powder batch, microwave assisted heating allows an active control of the temperature profile. As a consequence phase transformation is more homogeneous. This process related benefit as well as a possible enhancement of the diffusion process itself led to a reduction of processing time and/or process temperature. Finally this innovative technology can be used to influence the powder quality with respect to crystallite size while no effect was found to the particle or aggregate size derived from BET measurements.

5 Acknowledgement

We kindly acknowledge the financial support from the European Commission within the Contract G5RD-CT-1999-00088. We gratefully acknowledge L. Bonneau and S. Trombert, from Baikowski Chimie, France for supply of powder material and stimulating scientific discussions.

6 Literature

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