Energy and Cost Reduction with Heat Treatment of Ceramics

Introduction

Construction engineers select materials primarily with respect to function and costs. In addition, the carbon footprint of materials production is considered, since more and more companies have sustainability as targets or require eco labels for their products. Driven by the expectations of the consumers, a favorable carbon footprint will become an essential competitive advantage in the near future, even if no new regulations are enacted by public authorities. Fig. 1 shows the contributions from different parties to the consumption of primary energy in Germany: Industrial heat treatments need as much as 12 %; the relatively small ceramic industry uses 1,2 % of total energy. In the production of technical ceramics between 15 % and 45 % of energy is consumed during heat treatment [1]. The contribution of total energy cost to the added value of technical ceramics is relatively small. Even if the high energy cost of 3 ct/kWh and 10 ct/kWh for gas or electric power in Germany are considered. So the motivation for energy reduction during the heat treatment has been low in the past. This has resulted in a poor energy efficiency of current firing processes. Fig. 2 shows the ratio of the energy consumption, which is at the theoretical minimum to the actual energy consumption for typical ceramics. The energy efficiency is between 3 and 10 %. This has to be compared with an energy efficiency of 30 to 60 % achieved for the firing of clays [2]. The better energy efficiency during firing of clays is related to their larger ratio of ceramic heat capacity to heat capacity of kiln furniture. Furthermore it reflects the fact that the ratio of energy cost to added value is much higher for fired clays (10–30 % [1]) than for technical ceramics (5–10 % [1]). It is concluded that there is a large potential for energy savings in the heat treatment of technical ceramics (Fig. 2).

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Objectives

In a joint project called ENITEC, three ceramic companies, *CeramTec AG, Lapp Insulators GmbH & Co. KG* and *BCE Special Ceramics*, two furnace manufacturers, *Eisenmann Maschinenbau KG* and *FCT Systeme GmbH*, and two research institutes, *Fraunhofer ISC* and *Fraunhofer IWM*, are cooperating to minimize the energy consumption during the heat treatment of technical ceramics [4]. The energy consumption during the process steps drying, binder removal, sintering and finishing, is balanced in detail. Raw materials and forming processes are also considered to enhance sintering activity without causing a significant increase of energy consumption during the production of green components – e. g. during grinding. For heat treatment and finishing, a total reduction of 40 % in energy consumption is the aim. Heat treatments are investigated in continuously and discontinuously working furnaces. Exemplarily, different oxide and non-oxide ceramic components have been selected, covering the range between millimeters and meters of component size (Fig. 3). A number of energy saving methods is investigated in the project:

- Design features are identified by careful energy balancing to improve furnace construction.
- Processes like hot pressing or separate binder removal and sintering, which cost a lot of energy, are substituted or merged.
- Near net shape sintering is improved to minimize energy consumption during finishing.
- Methods to identify heating cycles with minimal energy consumption are developed.

The optimization of heating cycles is described in more detail below. Usually, with the heat treatment there is a trade-off situation between production quality on the one hand as well as energy savings and throughput on the other hand. A reduction of the heat capacity of kiln furniture, for example, leads to a large improvement of energy consumption, but also to reduced heat transfer within the firing load. As a result, larger temperature gradients can occur which lead to uneven product properties. Similar effects are caused by the increase of heating or cooling rates. A careful optimization of the process parameters during the heat treatment is required to identify the energy minimum without impairing product quality. A systematic approach is needed to perform this optimization in a sufficiently short time. Usually DOE methods (design of experiment) are used for systematic optimization of industrial processes [5]. Yet, for the present application, DOE is considered less efficient. During heat treatment a large number of parameters, such as heating and cooling rates, holding times, and temperatures, furnace atmosphere, and set up of ceramics and kiln furniture have to be optimized. These parameters are strongly correlated which leads to very large experimental designs. Instead of using DOE, the combination of accurate measuring methods and

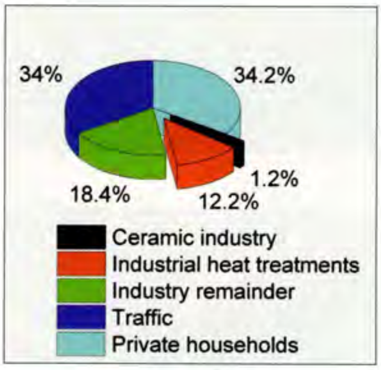


Fig. 1 Consumption of primary energy in Germany (Source: Arbeitsgemeinschaft Energiebilanzen, www.env-it.de)

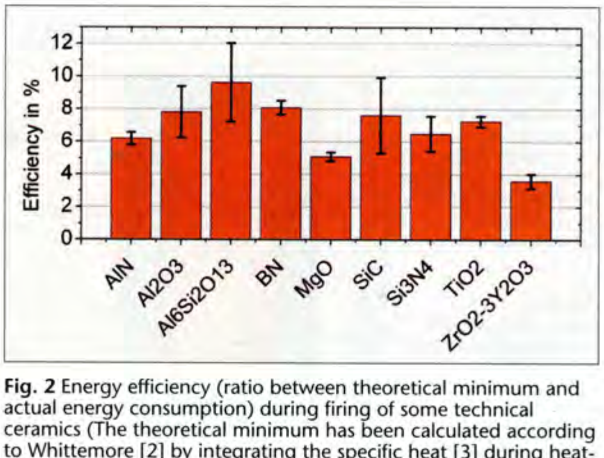


Fig. 2 Energy efficiency (ratio between theoretical minimum and actual energy consumption) during firing of some technical ceramics (The theoretical minimum has been calculated according to Whittemore [2] by integrating the specific heat [3] during heating of the ceramics; the actual energy consumption was extracted from a database [1])

Fig. 3
Some ceramics investigated exemplarily in the project ENITEC: zirconia ceramics for dental implants (upper l.), silicon carbide seal rings (lower l.) and porcelain high voltage insulators (r.)

computer simulation of the heat treatment is considered more suitable. This approach is described in the next two chapters.

FE Simulation of Heating Processes

FE methods are available for the simulation of heating processes which combine transient heat transfer by convection, conduction and radiation (e. g. [6]). Although the efficiency of FE simulation has been dramatically improved during the last decade, there are still some challenges when ceramic firing processes are simulated. The size of the models has to be strongly limited if reasonable computer time shall be achieved. For the optimization of energy consumption, many structural details of the furnaces and the firing load have to be simplified. The number of elements should be in the range of 10 000 to 100 000. So, complex small parts of the model are calculated separately to obtain effective heat transfer data within the submodel. In a multiscale approach the homogenized submodels are introduced into the larger model, sometimes in several hierarchical levels. Temperature and sintering state affect the effective thermal conductivity of the submodels. They are considered in the larger model by interpolating between different supporting points. As an example, Fig. 4 shows the temperature distribution in a cylindrical, graphite-heated top-hat kiln. The kiln was developed by FCT for the firing of silicon-carbide seal rings for the automotive industry. It has a vacuum tight water-cooled, stainless steel case and is isolated with rigid graphite felt. Argon is used as flush gas. The seal rings, which have a sintered diameter of 33 mm, are arranged in horizontal columns in several layers stacked within a cylindrical graphite container. The effective thermal conductivity of the columns in axial and radial direction has been calculated in a first step (Fig. 5). Using these data, the effective thermal conductivity of the individual layers in axial and radial directions has been calculated in the next step (Fig. 5). These data were introduced into the final furnace model (compare Fig. 4). The model is equipped with a virtual PID (Proportional Integral Differential) controller which controls the heating power in the graphite heaters according to the difference between set and actual temperature. So, preset time temperature cycles can be simulated. During the heat treatment simulations, the temperatures in the center and at the edges of the graphite container are recorded. The electrical power is integrated. Energy losses can be monitored in a virtual Sankey diagram [7]. Fig. 6a shows the temperatures and the electrical power during a heat treatment simulation close to the experimental standard conditions: heating and cooling rate = 2,5 K/min, holding time = 2 h at 2100 °C. The temperature difference between the center of the container and the edges is rather small (<10 K). The total energy consumption is 89 MJ/kg, which corresponds to a carbon footprint of 71 kg CO_2 per kg SiC. A reasonable agreement between simulation and experimental data within 10 % was achieved without any fitting parameters. Computer time was 20 min for the simulation of one heating cycle. Fig. 6b shows a virtual heating cycle with a much higher heating and cooling rate of 20 K/min using the same holding period of 2 h at 2100 °C. Now the total energy consumption is reduced drastically to 40 MJ/kg. The temperature difference between edges and center of the container has increased to 60 K. But it can be seen from the inserts in Fig. 6b that the temperature cycle for seal rings in the center is essentially equal to the temperature cycle for seal rings at the edges – apart

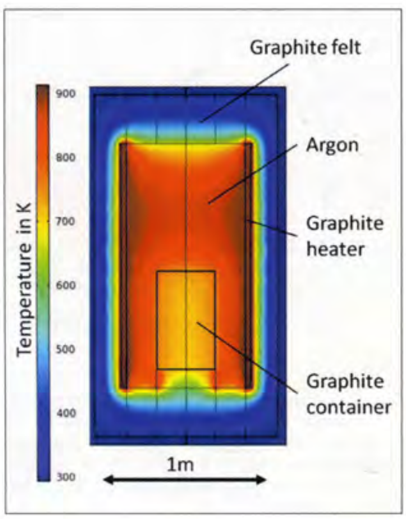


Fig. 4 (l.)
Cross section through a furnace used for sintering of SiC seal rings showing the simulated temperature distribution during heating (for testing purposes only 25 % of the furnace volume was used)

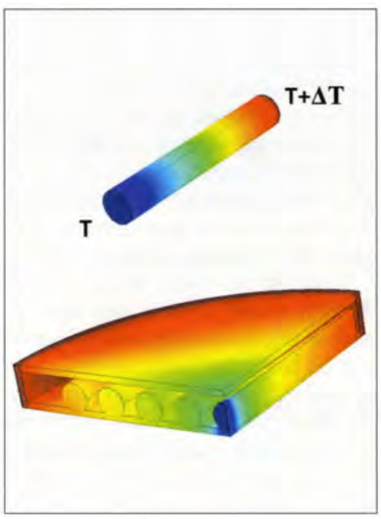
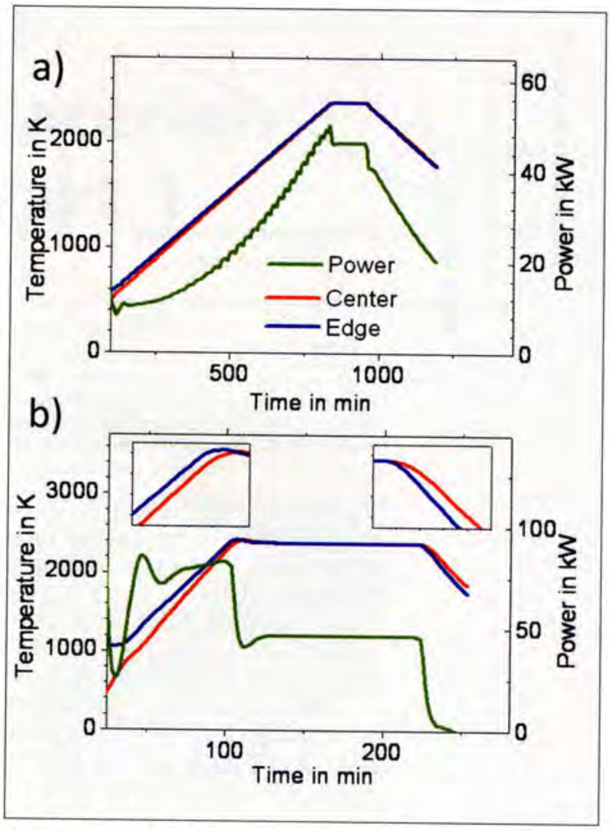


Fig. 5 (r.)
Submodels used for the furnace simulation shown in Fig. 4: columnar arrangement of individual SiC seal rings (top), arrangement of columns in layers (bottom)

from a time shift of 3 min. A constant time delay between interior and exterior components is considered not critical. The computer simulation suggests a drastic increase of heating and cooling rates in this application. In another simulation the thickness of the rigid graphite felt isolation was increased by 20 %. Energy consumption decreased from 89–78 MJ/kg. So with the FE furnace model different measures for energy reduction can be evaluated nicely. But other methods are required to predict the density and the quality of the sintered components.

Prediction of Material Behavior during Firing

The material changes during binder removal and sintering are rather complex. On the other hand accurate predictions of stresses and strains during the heat treatment are required for the identification of optimum process parameters. Therefore, a mixed approach is used: computer simulation is based on experimental input data obtained during the heat treatment. Special in situ measuring methods, so called thermooptical measuring methods (TOM) were developed for this purpose. They are available for heat treatments in oxidic (TOMMI+) and inert atmospheres (TOM-AC) and are described in more detail elsewhere [8]. The reproducibility of these methods is very high, which is a precondition for successful use in the optimization of heat treatments. As a measure for the reproducibility, the standard deviation of the measurand between different heat treatments, averaged over the heating process and scaled by its total change is suggested. Fig. 7 shows exemplarily three shrinkage curves of alumina green samples during sintering. The reproducibility of the dimensional measurement was 0,03 %, which is considered excellent. Weight changes are the most sensitive measure for binder removal. Using a commercial thermobalance (STA 449 C, *Netzsch*, Selb, Germany) and special precautions in sample preparation, a reproducibility of 0,1 % was obtained for the weight measurement. Based on these accurate measurements, the reaction rates for thermally activated processes like binder removal and sintering can be calculated according to the well-known kinetic field method [9]. The kinetic field is based on in situ measurements of the reaction rate for different but – during one heating experiment – constant heating rates. The kinetic field method can be used for a precise prediction of binder removal and sintering processes [10–12]. Figs. 8 and 9 demonstrate this exemplarily for the debindering and sintering of oxide ceramic green samples. The heating curves shown in black color were used to construct the kinetic field. The red curves in Figs. 8a and 9a show temperature cycles which were arbitrarily selected for a comparison of measured reaction rates and kinetic field simulation. An excellent agreement between simulation and experiment was obtained (compare Figs. 8b and 9b). So, based on the kinetic field technique the reaction rates can be calculated for any temperature cycle considered in process optimization. No other data than the in-situ measurements are required and no fitting parameters have to be matched. To obtain a complete description of material behavior during the heat treatment, more in-situ measuring methods are required. Fig. 10 shows a survey of methods which are most important for the optimization of binder removal and sintering, respectively. Thermal diffusivity measurements, for example, are necessary for an adequate simulation of heat transfer within the ceramics during heating. Note that thermal diffusivity changes by more than an order of magnitude during sintering. This has to be considered in the models. Acoustic emission is a useful tool to determine maximum safe heating rates during binder removal. The concept of maximum safe heating rates has been outlined in a previous paper [10]. The kinetic field has been implemented in the FE simulation of components behavior



Figs. 6a–b Simulated temperature curves and power consumption using heating and cooling rates of 2,5 K/min (a) and 20 K/min (b)

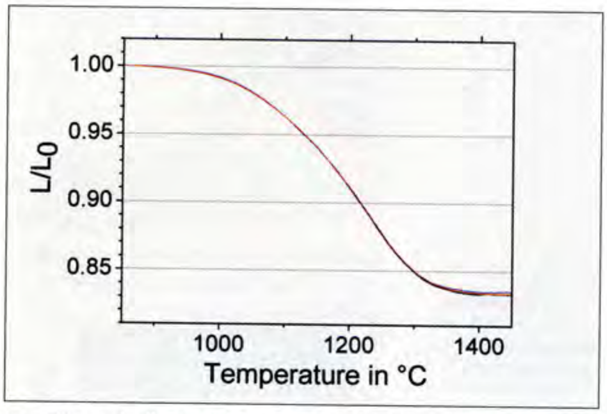
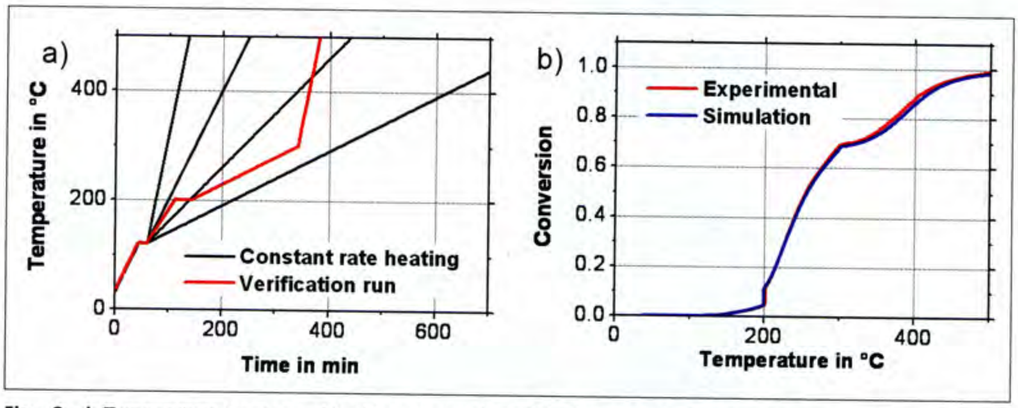
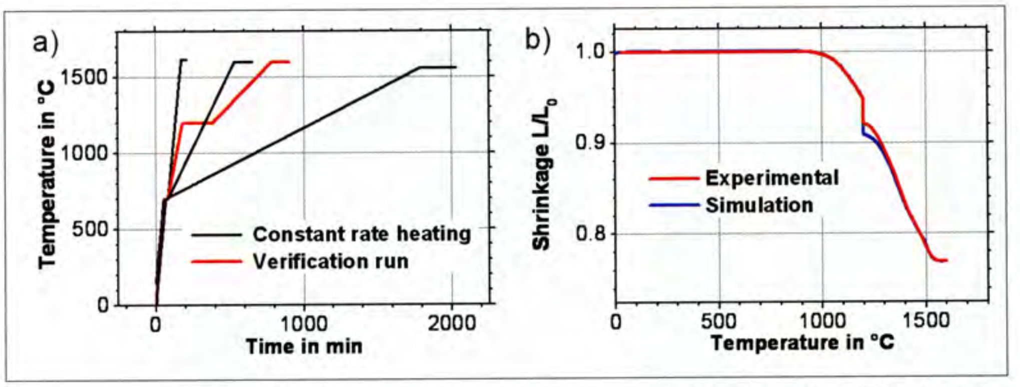


Fig. 7 Reproducibility test for sintering shrinkage measurements with thermooptical measuring methods using three alumina green samples



Figs. 8a–b Temperature curves used for the construction of the kinetic field during debindering of green samples and additional verification run (a), and comparison between measured and predicted weight change curve obtained in the verification run (b)



Figs. 9a–b Temperature curves used for the construction of the kinetic field during sintering of green samples and additional verification run (a), and comparison between measured and predicted shrinkage curve obtained in the verification run (b)

during heat treatment. This allows the prediction of the reaction rates of individual elements according to their thermal history, which is especially important when large components are sintered [12]. For small components the temperature cycles at individual positions in the furnace are extracted from the furnace simulation and directly used for a simulation of the final sintering state.

Summary

Although cost pressure is not large at the moment, a drastic reduction of energy consumption during production of technical ceramics is advantageous to fulfill expectations of the market for more ecological products. Since the energy efficiency of present heat treatments of technical ceramics is very low, large improvements are possible. In the joint project ENITEC, amongst others, methods are developed to minimize energy consumption during the heat treatment of ceramics. A systematic approach has been suggested to identify optimum process parameters in the trade-off situation between energy consumption and production quality. It is based on a coupling between accurate in-situ measuring methods and computer simulations. In the remaining period of the ENITEC project, the efficiency of the methods will be improved to enable a fast transfer to other ceramic heat treatments. In addition to energy savings, higher throughput can be obtained by the new approach. Usually, the increase of throughput has a large impact on production costs due to the amortization of furnaces. In the future sustainability will be profitable for the ceramic industry.

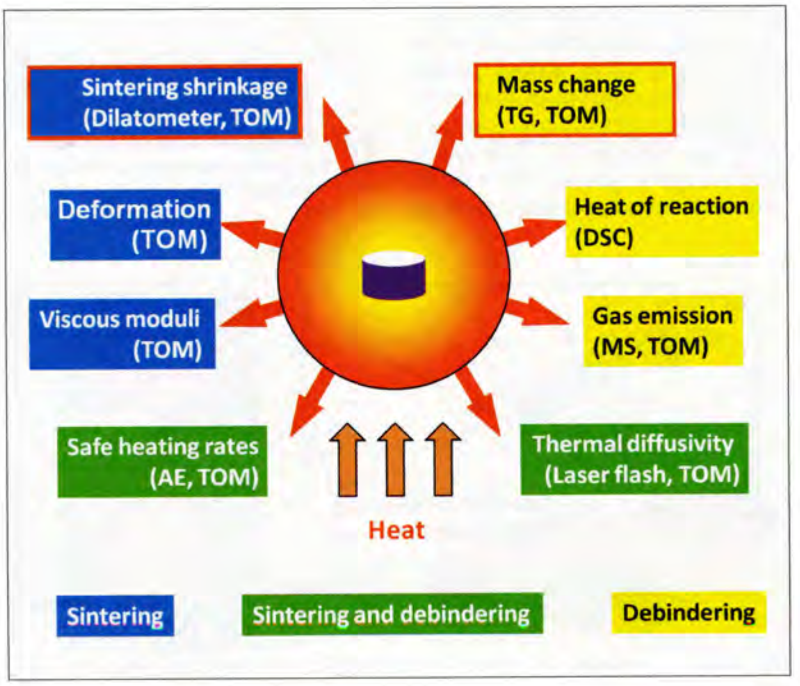


Fig. 10 In-situ measuring methods used for the optimization of heat treatments (TOM = Thermo-optical measuring methods, TG = Thermo-gravimetry, DSC = Dynamic scanning calorimetry, MS = Mass spectrometry, AE = Acoustic emission)

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