Sustainable Thermal Processes in Ceramic Production

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The experience of the last two years of economic instability has clearly demonstrated how critical energy efficient processes are. Both the limited availability of energy as well as the monthly shock of the energy bill have led to huge challenges and changes in production planning and economics. Solutions on how to reduce energy consumption and how to make thermal processing more efficient and reliable are explained by the following examples.

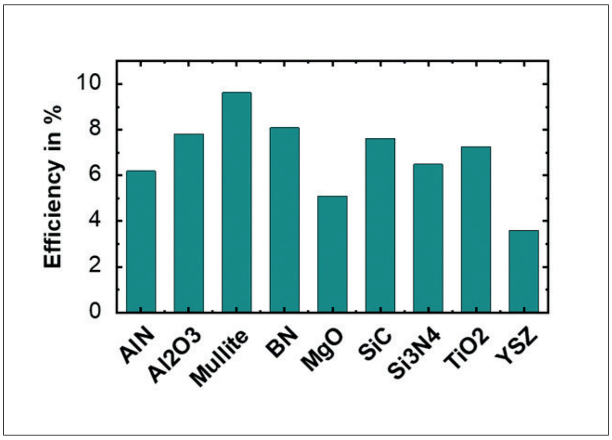

Fig. 1 Efficiency of sintering processes for selected technical ceramics

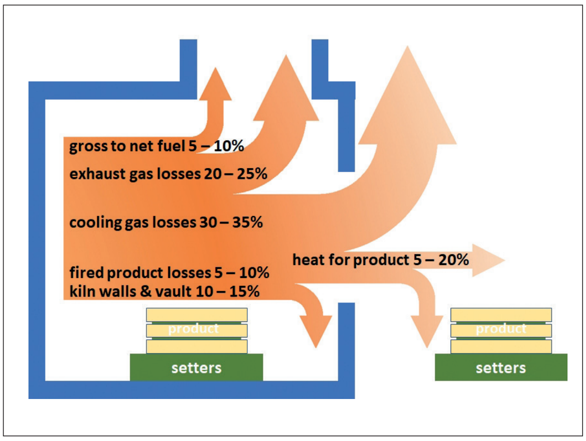

Fig. 2 Energy losses in a ceramic tunnel kiln for tile production, adapted from [1–3]

Introduction

In ceramic processing, the thermal processes play a particular role. Depending on the process and the product, about 35–75 % of the energy required for the production of ceramics is required for the heat treatment [1]. On the other hand, the energy efficiency, defined as the ratio of the theoretical energy required for achieving the sintering temperature to the actual energy input in ceramic processing, is still at a very low level. For technical ceramics, it amounts between 5–10 % (Fig. 1).

Energy losses have different origins [1–3]. As sketched in Fig. 2 for a continuous kiln for tiles most of the energy is lost through insulation, cooling and exhaust gas. In batch furnaces, the losses are even higher unless special care is paid to heat recovery. However, there are several starting points for improving the energy efficiency even with little investment required. As a first step, heating cycles that are strictly based on the requirements of the product and the oven usually allow energy savings in the range of 10–20 % [4]. For many older kilns, there is also huge potential for savings through a comprehensive analysis of the heat flows and identifying the origins of heat leakage. From this, a targeted design of the insulation and gas flow is a useful step for improvements and savings. Besides the losses through the kiln walls and the exhaust gas there is huge potential in optimizing the kiln furniture, which often requires more energy than the product itself. For batch as well as for continuous kilns the kiln furniture is a necessary but costly component with regard to energy consumption. The energy for heating it can only be partially recovered during cooling. By using kiln furniture with reduced heat capacity and optimized thermo-mechanical design this waste of energy can be reduced. Moreover, thermal buffering by the kiln furniture is reduced, making heating processes more flexible and controllable.

Due to the increasing cost of CO2 emissions, alternative heating methods such as resistance heating and hydrogen combustion using regenerative energy sources are gaining in importance. The fluctuating availability of

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regenerative energy requires higher flexibility of industrial furnaces in terms of demand side management. However, one has to be aware that a change in the energy source is a major intervention, affecting a multitude of aspects. For example, besides installation issues, a change from gas to electric heating fundamentally alters the ratio of heat transfer via convection, conduction and radiation. This also changes the gas phase reactions between the charge and the furnace atmosphere - e.g., during debinding. In open flame processes the charge and the refractory materials are in direct contact with the combustion atmosphere which may contain different proportions of CO_2, CO, H_2O, H_2, NO_x, N_2, SO_x and/or hydrocarbons, which can chemically react and modify the heating processes. Therefore, before switching the heat source, the interaction of the heat source with the materials and its influence on the thermal conditions in the oven has to be considered.

The response of a material to the heating cycle and the influence of the gas atmosphere can be predicted by a systematic approach to the debinding and sintering behavior, developed at the HTL [5, 6]. Based on digital twins, representing a description of the furnace with all heat flows, the effects of heating methods and other measures for CO_2 reduction are determined [7]. So, efficient instruments are available to improve energy efficiency and to adapt to new heating requirements. Examples of how to master the current and future energy-related challenges in ceramic processing are described in the following paragraphs.

Improvement of process parameters of heat treatment

Considering the long lifetime of industrial furnaces and the high costs for modifications in the furnace, the implementation of optimized heating cycles is the simplest and most direct way to increase energy efficiency. Moreover, this optimization is used to improve product quality and to reduce scrap. As a starting point and prerequisite for the optimization of heating profiles, the properties of the material as a function of temperature and thermal history have to be known. For this purpose, standard procedures have been developed at the HTL with which all relevant data can be determined in a time and cost-efficient way [6, 8].

The basis for optimization is the so-called kinetic-field [9]. It allows to calculate the decomposition or compaction rate of a ceramic green body as a function of the thermal history on the basis of simple debinding or sintering curves with a constant heating rate. Other temperature and thermal-history-dependent properties such as thermal conductivity (which changes with loss of organics and the formation of sinter necks), gas permeability, mechanical strength and viscous moduli are measured regarding the specific process. Then, the parametrized measuring data are used in coupled thermomechanical Finite Element (FE) simulations. They provide optimized heating cycles even for large components of more than 0,5 m^3.

Optimization can be performed on both low and high temperature processes. There are hardly any restrictions with regard to the atmosphere, as almost all atmospheres that are commonly used in ceramic manufacturing processes can be realized in the laboratory furnaces at the HTL. For example, optimized heating profiles for debinding/pyrolysis and sintering could be successfully determined for oxide ceramics such as Al_2O_3, ZrO_2 and their mixtures as well as for SiC, AlN and Si_3N_4 [1, 4].

In debinding/pyrolyzing, the fundamental aim is to create the fastest temperature cycle that can be used to reliably produce defect-free components. The focus is particularly set on the stresses caused by the gaseous decomposition products of the binder and by thermal gradients because of the limited mass and heat transfer inside the components.

Due to the low mechanical strength of the parts in between binder burn-out and sintering neck formation, critical stresses must be avoided. The temperature distribution in the stack can be taken into account by additional FE-simulation. Details on the steps and how to work most efficiently have been presented in more detail in previous articles [5, 8].

In the case of sintering, the focus is set on process-economy (throughput and energy savings) and product quality (avoidance of scrap and near net shape performance). One critical point is deformation at higher temperatures due to creep caused by gravity and friction or due to inhomogeneous shrinkage caused by temperature gradients. In the FE-simulations this is considered by using viscous moduli. Their measurement is difficult, but the special thermo-optical measuring equipment at the HTL allows to determine these moduli during sintering by means of adapted cyclic loading tests [6].

Utilization of user-apps

As mentioned above, the processes and procedures that are required for optimizing thermal processes are well described in previous publications and have proven as very beneficial in a multitude of industrial implementations. However, one request that has been expressed from industrial users more frequently in the last years has been to be able to work autonomously when changing the geometry of the product or adapting the furnace processes. This also allows highly confidential products and processes to be implemented in house without consultation from external partners.

Recently, the provider of the FE-software (COMSOL) used has introduced an opportunity to link user defined FE models to stand-alone programs. This allowed the HTL to develop so-called user-apps. They are based on the FE software, but do not require a separate license from COMSOL. We implement all the required measuring data of the specific green material and the respective coupled thermomechanical FE model in the app and delivered to the end user. They can then independently adapt and optimize their furnace processes within wide limits of component geometries and time-temperature cycles.

Depending on the user’s interest, temperature distribution, stresses, degree of debinding respectively sintering can be calculated for the 3D-model of the green compact and inspected during the heat treatment. New part geometries can be implemented through a CAD-interface. A screenshot of the debinding app with a 3D-printed HTL-logo is shown in Fig 3, showing pressure variations.

Effects of substitution of natural gas combustion by other heat sources

Intensive work is currently focused on CO_2-neutral heating methods. The approaches that are pursued are manifold. When looking at the national and European programs, both the use of pure hydrogen - or in admixtures to natural gas during a transition phase – as well as heating with resistors, induction or microwaves are addressed in recent calls.

Where the paths will lead is still an open question and specific solutions may be selected depending on the individual process requirements. In any case, it is important to keep in mind that when changing the heating method not only the heat transfer is changed (proportions of convection, heat conduction and radiation) but also the chemical composition of the furnace atmosphere is altered. This can have a decisive influence on the debinding and sintering process.

For example, when using electric heating in debinding ovens, air is the common furnace atmosphere which contains varying portions of decomposition products from debinding (CO, CO_2, H_2O, possibly hydrocarbons). In natural gas fired furnaces, depending on the λ value, the main components are N_2, CO/CO_2 and up to 18 % of water vapor, the latter being present due to the combustion reaction of hydrocarbons. Even higher water contents of 35 % or up to 100 % are reached when hydrogen is burnt in air or when oxygen is used instead of air in the so-called oxy-fuel process with H_2.

An important point is the presence of water steam, which can have catalytic effects during debinding and thus affect the debinding rate. In addition, the interaction of water molecules with oxidic particle surfaces is known to influence the subsequent sintering process due to the formation and removal of OH-groups [11].

If these effects are not taken into account, the risk of incompletely fired or deformed products will increase enormously. Particular care has to be taken when densification takes place via a melt phase, such as in the case of porcelain. Moisture from the oven atmosphere can be dissolved in the melt and reduces the viscosity. Rearrangement and recrystallization processes are altered and the densification behavior changes.

To gain a better understanding of the influence of the furnace atmosphere on the material behavior, debinding and sintering processes are investigated at the HTL using so-called Thermooptical-Measuring (TOM)-furnaces. These specially developed devices allow the adjustment of the gas composition during the heat treatment. They enable optical dilatometry, thermogravimetry or controlled load applications (with respect to softening and creep). For example the TOM-furnace, TOM_2 is a resistance-heated furnace in which, in addition to the common gases (CO, CO_2, N_2, synth. air, inert gases), water steam concentrations of up to 100 % can be selectively introduced into the oven chamber, whereas the TOM-furnace (Fig. 4a), TOM_metal can be operated with 100 % hydrogen or inert gases at up to 30 bar (Fig. 4b).

As an example, Fig. 5 shows the influence of the furnace atmosphere on the sintering behavior of porcelain. The curves show the densification behavior at a constant heating rate of 3,5 K/min up to 1200 °C (a) in air, (b) simulated gas-combustion atmosphere and (c) simulated hydrogen gas-combustion atmosphere. Oxygen was provided in the form of synthetic air, CO_2 and H_2 as well as the water vapor were introduced via a gas mixer. In addition, the atmosphere was set to oxidizing (< 1000 °C), reducing and neutral conditions by adjusting the fractions of oxygen and hydrogen.

Without going into detail one can clearly see that the atmosphere has a significant influence on the densification behavior. The sintering shrinkage is strongly reduced

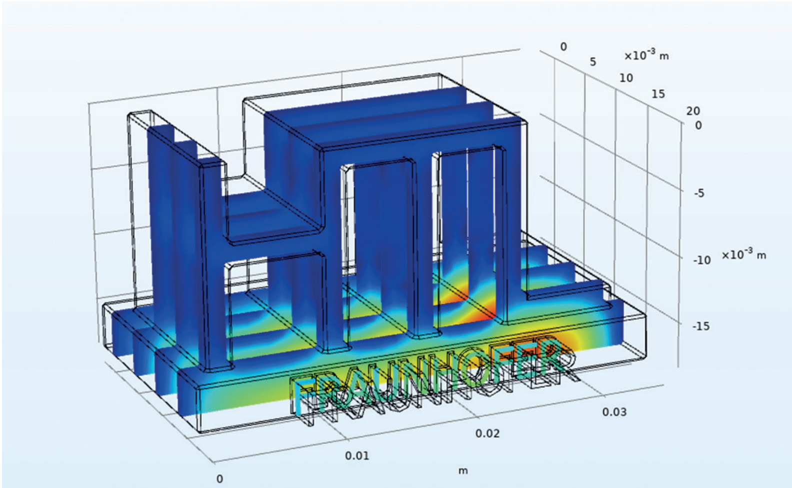

Fig. 3 **Screenshot of the debinding user-app for optimizing time-temperature cycles**

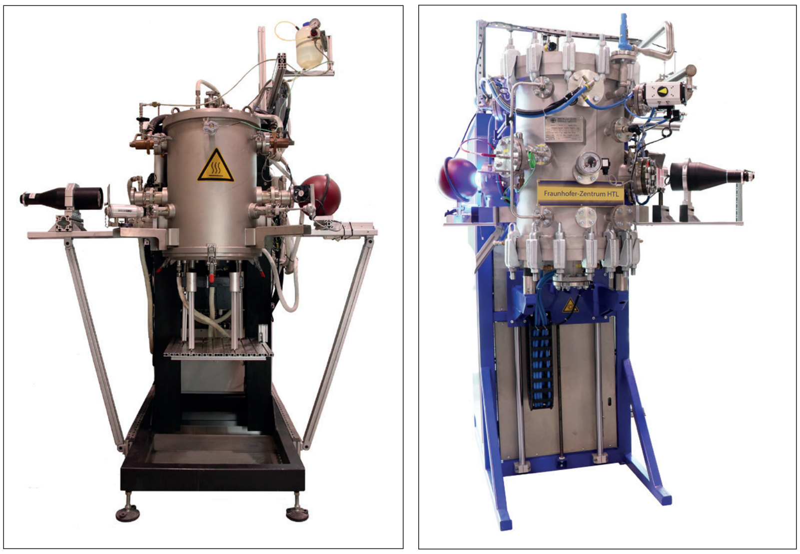

Fig. 4a–b TOM_2 **(l.) is a thermo-optical measurement device for investigating the influence of gas atmospheres (in particular the effect of water steam) on the debinding and sintering behavior of ceramics using thermogravimetry and optical dilatometry; TOM_metal (r.) is a thermo-optical measurement device that allows investigations in 100 % hydrogen atmosphere or inert gases of up to 30 bar**

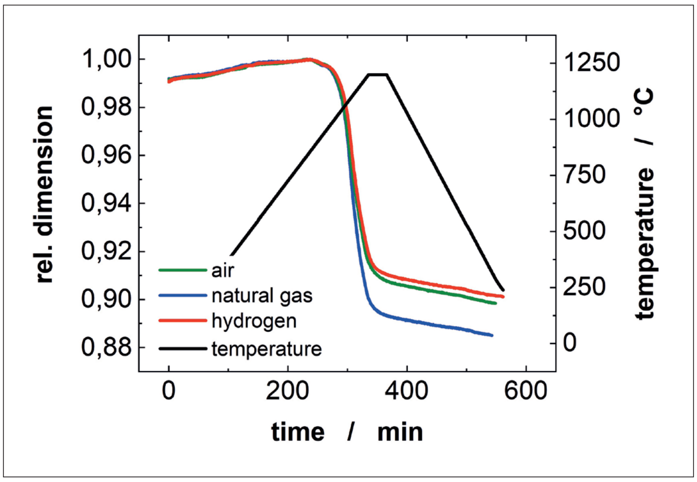

Fig. 5 Shrinkage curves for a porcelain material in air, simulated natural gas combustion atmosphere and simulated hydrogen combustion atmosphere

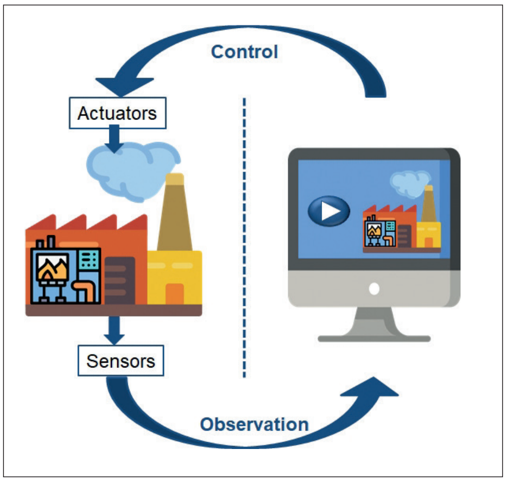

Fig. 6 Schema of the imaging of the industrial furnace in the computer model as a digital twin

when switching from simulated gas-firing atmosphere to electrical heating in air. In the case of the simulated hydrogen combustion gas the behavior is even more complex.

Digital twins of production furnaces

Heat management within the industrial furnaces can be considerably improved using digital twins which reflect the relevant heat flows by convection, heat radiation and conduction in a computer model (Fig. 6). Usually FE and Computational Fluid Dynamic (CFD) methods are used for this purpose. A digital twin of a tunnel kiln for the production of sanitary ware has been presented recently [7].

A particular feature of the digital twin developed at the HTL is the coupling of the digital furnace model with the debinding and sintering models for the charge described in the previous sections. This coupling allows a direct evaluation of changes in the furnace set-up and the process parameters on the product quality. Moreover, digital twins will support a demand side management of production furnaces where the energy consumption can be adapted to their availability.

However, a critical aspect in the development of digital twins is the validation of the input data and the simulation results. In order to do so, several approaches have been started at the HTL in the project DiMaWert [12]. Here, high temperature material properties are measured using special TOM-furnaces. In particular, emissivity, thermal conductivity and specific heat can be determined for refractories up to temperatures of 1750 °C [13]. Moreover, thermal cycling and thermal shock properties are measured in a special way to evaluate materials for high temperature operations [14]. In addition, special test set-ups have been developed to separately investigate the heat transfer via convection, heat radiation and conduction.

As an example, Fig. 7 shows a set-up for measuring the heat transfer between samples and a gas with a well-defined velocity in a flow channel. By measuring the temperature distribution on the samples, which can be flexibly placed in the path of the gas flow, the CFD model and the assumptions about the heat transfer between gas and samples are validated. Similarly, heat radiation models are validated using a radiation channel with samples which can be placed at various positions. Heat loss through the insulation of the furnace walls is determined using a measuring furnace, in which a segment of the wall is replaced by the testing material. This allows the models for heat conduction and radiation through multilayer isolations are validated.

To validate the digital twin of industrial furnaces and to obtain additional information, it is also crucial to have precise measurement data from the kiln. For this purpose, advanced sensors that, in addition to temperature, also allow the measurement of the gas composition, gas and radiative flows inside the furnace are also currently being developed in the DiMaWert project at the HTL [12]. They can be installed permanently in the furnace or work as mobile, stand-alone sensors to measure data during a furnace run (Fig. 8).

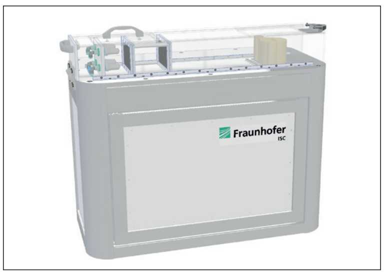

Fig. 7 Experimental measurement set-up for the validation of FE-simulations on convection for thermal management and furnace optimization

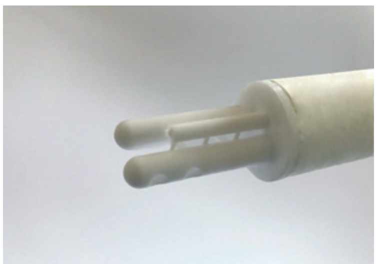

Fig. 8 Ceramic sensor head for measuring gas flow and temperature in high temperature furnaces

Components for improved heating processes

Based on the information from the digital twin simulations and the measurements in industrial furnaces, optimized designs and

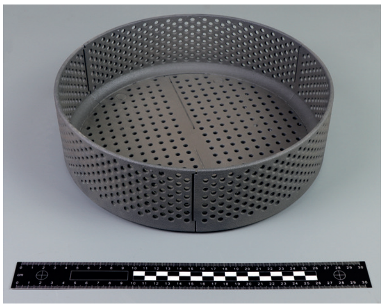
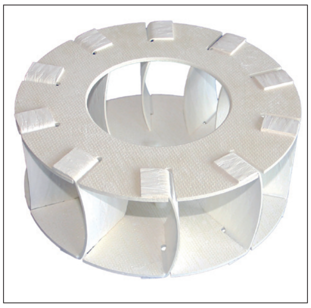
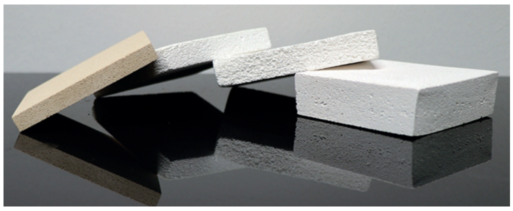

Fig. 9 **High temperature stable light-weight components: SiSiC-setters (l.), O-CMC impeller (middle), and oxidic foams (r.)**

set-ups are established. This allows a precise definition of the requirements for new high temperature components. Example as shown in Fig. 9 are high temperature fans which are designed for enhanced gas circulation.

At the HTL impellers made of oxidic ceramic matrix composites are being developed. They combine excellent high temperature and corrosion resistance with a high fracture toughness [15]. Other examples are special ceramic foams which are designed as furnace insulation according to the required operating temperature and thermal resistance [16]. Light-weight kiln furniture has been developed based on tri-modal particle size distributions and high porosity. Systematic optimization was achieved using material indices together with measurements of the creep behavior [17].

Further improvements for specific applications are currently being addressed by simulation assisted topology optimization [18]. One means for realizing such optimized structures are fast working 3D-printers. For example, lightweight setters made of SiSiC for pyrolysis runs were realized by binder jetting of SiC powder and subsequent melt infiltration of silicon melt.

An important step for optimizing their production was to split the setter into separate parts which are bonded together in the silicon infiltration step. By this, packing density could be considerably increased during 3D printing.

Summary

There are several options on how to reduce energy consumption and to make thermal processes more sustainable, now and in the future, even with very little investment. A pre-requisite is a comprehensive knowledge of the response of the charge and the furnace when temperature cycles, set-up or energy sources are varied.

Process parameters can be optimized by the operator himself applying special user apps which are based on debinding or sintering models of the respective ceramic. Special care has to be taken with respect to the furnace atmosphere – especially in the case of water steam – which can have a critical influence on the process and the material quality.

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