New Techniques for the Determination of Refractory Material Properties at High Temperatures

G. Seifert, V. Schmitt, F. Raether

The expected service life of refractories is an important issue in almost any kind of high-temperature processes in industry. Fostered by the political regulations to improve energy efficiency and reduce CO_2 emissions, research activities on refractories have been intensified recently. To enable reliable lifetime prognoses, theoretical modeling is as important as the availability of precise high-temperature data on the material behaviour against thermal shock and corrosive agents. In this work, two new thermo-optical measuring devices are introduced which provide extended capabilities for studies of thermal shock and thermal cycling behaviour of refractories and their degradation by corrosive gases or abrasive particle flow.

1 Introduction

The reliable prediction of refractory material lifetimes is of great interest for any industrial area using thermal processing at high temperatures. E.g., it is crucial to avoid unforeseen interruptions or even damage and complete breakdown of large production lines. Another aspect, becoming more important nowadays, is the energy efficiency and carbon dioxide footprint of thermal processes. On the basis of validated lifetime assessments, it is possible to select the most stable and long-lived refractory material for any special thermal processing situation. Typically this is done when designing new or reconfiguring existing furnaces. Lifetime assessments enable industrial users to stick to the regulatory framework and, in particular, reduce the energy consumption and costs of the respective production process.

From the research point of view such predictions are, however, a very challenging task: predictions have to account for the special conditions of the thermal process considered (such as thermal shocks, thermal cycling or strong thermal gradients) on one hand, and resistance against potentially corrosive atmospheres on the other hand. Furthermore, on the "macroscopic" side of the problem there are conditions defined by the practical processing situation in sometimes very large industrial kilns, where the actual temperatures and gradients can hardly be measured. On the other end the – mostly inhomogeneous – microstructure of the refractory material is the key parameter to understand the crack and damage behaviour in detail. Thus, any kind of lifetime estimation or prediction first requires a well-founded either theoretical or heuristic approach to qualify the service-life of a refractory component from the as-delivered material or by a standardized test, respectively. Secondly, however, even the best theoretical prognostic method can only be of practical use when all material parameters and their temperature dependence are known precisely up to operation temperatures. Also, the predictions of the model are only reliable when they can be verified by measurements of the materials' reaction to the realistic thermal loading conditions.

This paper is giving a brief overview of established and upcoming lifetime estimation methods for refractories. Then it describes the state-of-the-art of measuring thermal shock or cycling behaviour of refractories and their chemical modifications by corrosive gases at high temperatures, focusing on two new experimental systems at the Fraunhofer Center HTL in Bayreuth (Germany).

1.1 Established techniques to characterize refractory lifetimes

In order to characterize thermal shock resistance and, in particular, to enable predictions of the lifetime of refractory components, a number of experimental techniques and theoretical models have been developed. Common goal is to assess the failure probability caused by strong temperature gradients or transient thermal stresses, expected under operating conditions. The classic thermal shock parameters allow a relative ranking of different materials by using a combination of known material properties (such as modulus of elasticity, fracture toughness, thermal expansion coefficient, etc.) [1, 2].

Standardized methods for thermal shock tests are performed by cooling a hot brick from, e.g., 950 °C (DIN EN 993-11) fast to room temperature by water or compressed air; after a defined number of such cycles the degree of damage is being assessed with different methods. As an example we exposed two different half bricks (bauxite Alurath B80 and alumina spinel Alurath SP78) to five cycles with air cooling. The

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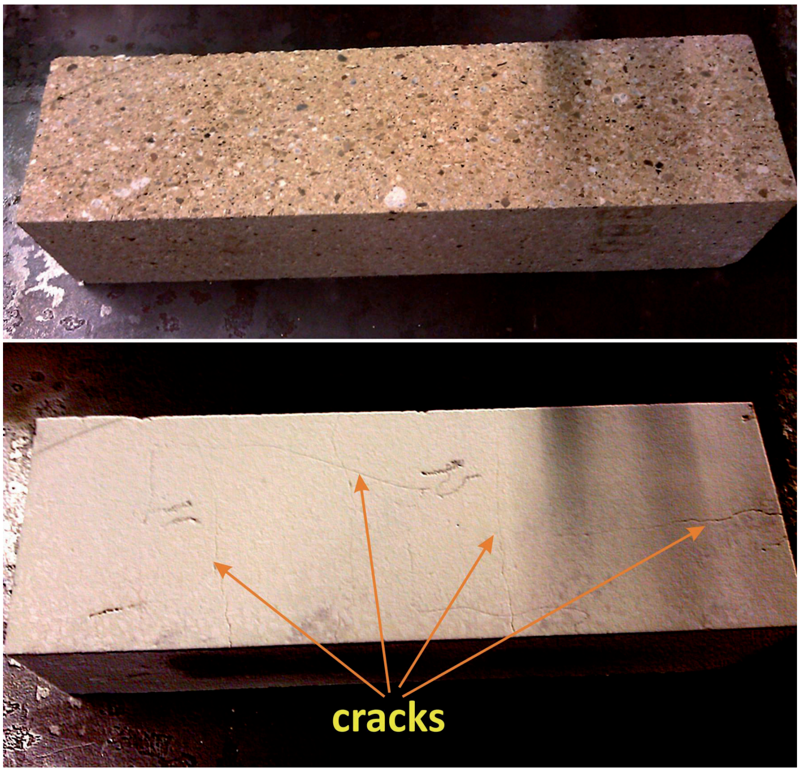

Fig. 1 **Refractory bricks after 2 cycles of a standardized thermal shock test; top: bauxite B80; bottom: alumina spinel SP78**

SP78 had visible cracks at its surface already after the second cycle (Fig. 1) and broke into two pieces during the fourth, while the B80 brick showed no visible damage after 5 cycles. The ultrasound velocities of the two materials after 5 (or 4, respectively) cycles were decreased by 9 % (B80) and 54 % (SP78), nicely reflecting their apparently very different crack density. These results insofar allow a general thermal shock resistance ranking of the two exemplary refractories, but do not give any information as to the processes of crack initiation and propagation. Nor can they be simply transferred to thermal processes where, e.g., a thermal shock in the range between 1100 °C to 1500 °C occurs.

Overall, neither the thermal shock parameters nor the mentioned standard thermal shock tests can provide a quantitative forecast of service life for different load scenarios.

A further, long-established approach is to acquire an estimate of the distribution of fracture-initiating defects in a material by mechanical strength tests using the Weibull distribution (see for example [3]). This usually requires a statistically relevant number of, e.g., bending fracture tests (varying specimen geometry, temperature, load increase velocity, etc.). Then the fundamental assumption is made that always the weakest point triggers the rupture leading to component failure ("weakest link theory"). With this prerequisite, a forecast of the probability of failure of a component as a function of time under a defined load can be derived from the measured data. The method has two difficulties: firstly, a suitable failure model has to be available for the particular material; secondly, numerous experiments are required for a reliable, statistically validated conclusion. Furthermore, the required material parameters in the high temperature range are often not known at all, or at least cannot be measured with sufficiently high precision [4].

However, if the Weibull parameters are known with sufficient accuracy the method is very powerful. In particular, service life prognoses can be up-scaled for arbitrary components made of the respective material and applied to a variety of impact scenarios by means of finite element methods (FEM) [3]. To make this approach accessible to a larger audience, in the early 1990s NASA has developed a software package called CARES/life (ceramics analysis and reliability evaluation of structures), in which different models for lifetime predictions are implemented. The package includes interfaces to commercial FEM packages for component-related predictions. It is commercially available now along with software (called WeibPar) for the statistically optimized estimation of the Weibull parameters from experimental data (see: www.ceramicreliability.com/software/). To simplify matters the Weibull parameters are usually measured at ambient temperature. Note that misinterpretations may occur if critical faults are different at operation temperatures of the refractory materials.

1.2 Novel approaches towards improved service-life prognoses

In recent years, novel procedures have been developed to theoretically describe and experimentally detect crack initiation and propagation upon thermal cycling. These methods are often based on the dependency of ultrasound velocity on the number and size of cracks in the material. For instance, Boccaccini verified the "cumulative flaw length theory" [5, 6] for two cordierite-mullite type refractory plates having different thermal-shock failure mechanisms – one type showing early crack initiation and slow crack propagation and the other type delayed crack initiation and fast crack propagation [7]. With this approach, the lifetime of the refractories is estimated by measuring and evaluating the distribution of ultrasound velocities in the as delivered state. Other approaches use the change of ultrasound velocity after a thermal shock cycle to define special damage parameters; these parameters are then used to identify critical spots in refractory components by help of FEM under the expected thermal loading conditions [8, 9].

Finally, there are fundamental research activities addressing the problems of crack initiation and propagation on a theoretical level to understand in detail the dynamic behaviour of propagation of an individual crack in a particular material. Recent work comprises approaches based on continuum theories [10] as well as complex multi-scale FEM simulations [11]. One important recent finding was that the temperature dependence of the material parameters (here bulk modulus) has a strong impact on the crack propagation speed [12]. Thus, future predic-

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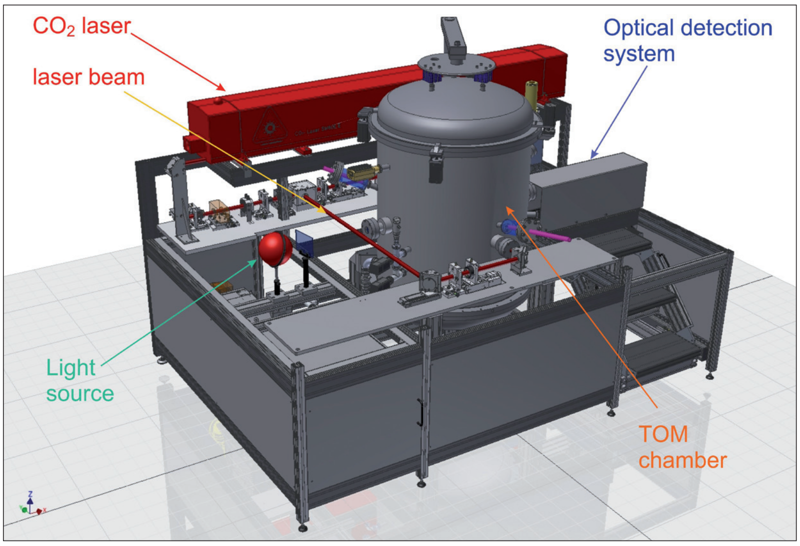

Fig. 2 3D layout of TOM_wave

Fig. 3 Photograph of TOM_wave

tion techniques for refractories service life will be relying on the precise knowledge of high-temperature material data.

2 Experimental techniques

There is a broad variety of commercially available devices and methods to cover the demand for precise high-temperature data on refractories. Compact stand-alone devices are available for measuring, e.g., fracture toughness, elastic moduli, thermal conductivity, coefficient of thermal expansion etc. More specialized experimental techniques are made for studying the thermal shock and corrosive behaviour of refractories in laboratory scale measuring devices, but nonetheless under industry-relevant conditions. The compact devices are always limited with respect to either maximum sample size or maximum test temperature or measuring accuracy. Since the specialized techniques go beyond these limitations, they mostly require complex experimental setups and pertinent expertise. That is why they are usually offered in form of a characterization or calibration service by test laboratories, research institutes and universities.

A particular approach is the use of thermo-optical measuring (TOM) devices, which allow monitoring any kind of shape change of a sample with high precision during thermal processing. This enables contactless determination of parameters like thermal expansion, creep or shrinkage. The team of Fraunhofer Center for High Temperature Materials and Design (HTL), which has a long-standing experience in development, use and metrological improvement of TOM devices [13, 14], demonstrated very recently an optical resolution of 0,1 µm, which enables measurements with unprecedented accuracy. Adding additional equipment to the TOM chamber, further information on the sample behaviour during thermal processing can be obtained (e.g. scales for weight changes or microphones for crack detection). Following this path, two new TOM devices, called TOM_wave and TOM_chem (explanation see below) were developed for the particular needs of assessing the service life of refractories. These two devices, the concepts and capabilities of which will be described below, are currently being finalized and calibrated in the laboratories of Fraunhofer HTL, and will be in full operation by the end of 2015.

2.1 Setup for determination of advanced thermal shock properties – TOM_wave

TOM_wave is a measuring system which provides thermal shock or thermal cycling conditions like in the real industrial application. It determines the degree of damage in a refractory component not only after the whole thermal loading cycle, but at any point of time during the loading process. Furthermore, TOM_wave is designed for measuring thermal diffusivity of large samples of some tens of cubic centimetres using a novel laser-flash technique. The suitability for such large sample volumes is essential in the investigation of refractories, because their heterogeneous microstructures would otherwise prohibit reproducible measuring results. The system is an improved and extended version of previously developed devices using halogen lamps for fast sample heating and laser-flash measuring in a separate furnace; these devices are now installed at ECREF in Höhr-Grenzhausen (see www.ecref.eu/index.php?id=projekte).

Figs. 2, 3 show in a rendered 3D representation and a real photo how the above requirements have been realized in the TOM_wave device at Fraunhofer HTL. Key component is a 600 W CO_2-laser, visible in red at the rear of the setup. The laser beam (also printed in red) is guided into the TOM furnace, which provides a controlled atmosphere – including vacuum – at temperatures up to 1750 °C. The CO_2 laser

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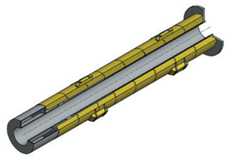

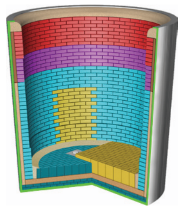

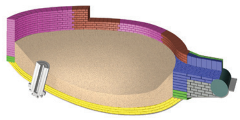

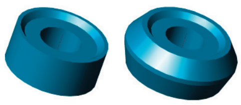

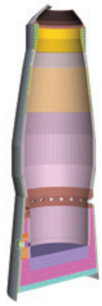

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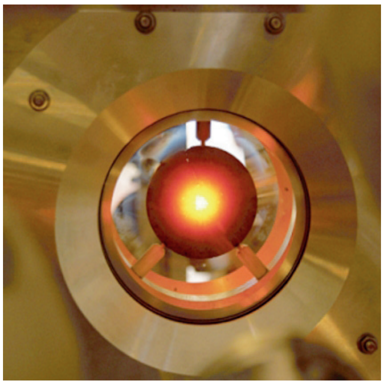

Fig. 4 Laser-heated sample in TOM device

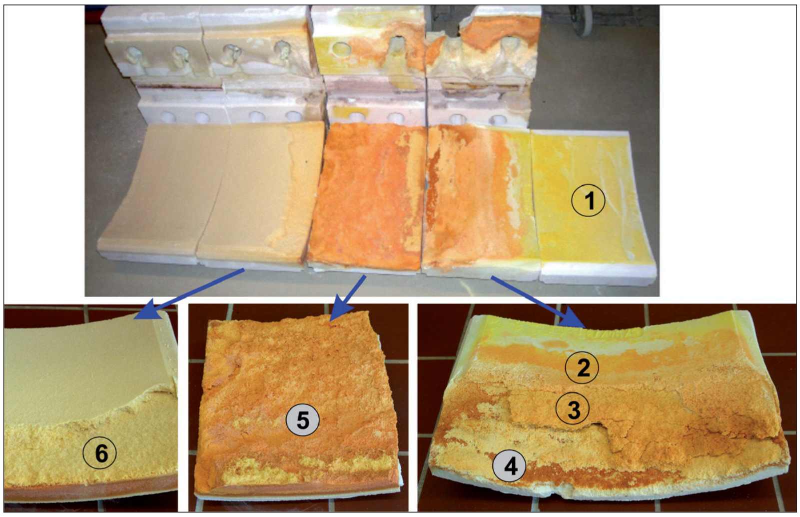

Fig. 5 Corrosion of mullite-based refractory form components after exposure to PbO- and S-vapors; numbers identify different zones as specified in Tab. 1

radiation can be used to provide additional heating of the (disc-shaped) samples from one or two sides, with beam diameters variable between 2 mm and 20 mm. Fast ramps between 0 % and 100 % of laser power are available for thermal shock and thermal cycling experiments; pulsed operation is also available and can be used for laser flash measurements and thermal excitation for self-oscillations. In addition, optical imaging enables measurement of thermal expansion of the sample, and an IR spectrometer covering a wavelength range from 0,9 µm to 28 µm detects spectral emissivity of the sample.

Inside the TOM furnace, several detectors accomplish the setup: two pyrometers measure the temperatures in the center of the sample and on their outer rim. Thus, using the CO_2 laser as heat source in the sample center (Fig. 4), the thermal conductivities in axial and radial direction can be obtained independent from each other. For the determination of these material parameters, an inverse FE simulation of heat conduction based on a 2½-dimensional model is used. For acoustical detection, four microphones are placed inside the furnace vessel. Noise of other sources than the sample is effectively suppressed by a sound tracking system operating in real time with a maximum frequency of 100 kHz and a resolution of 1 cm. Thus the acoustic system is able to detect signals of cracks during thermal shock or thermal cycling experiments. Another application is the acoustic analysis of laser-induced self-oscillations. The resonance frequency of these oscillations yields Young's modulus of the sample, while the width of the resonance peak is related to the crack wall friction and reflects accumulated damage of the sample. Thus using TOM_wave, thermal loads can be applied for the first time in a wide variety of well-defined time and temperature ranges between ambient temperature and 1750 °C. Damage is recorded instantaneously and all other thermal parameters required for the up-scaling of results to service conditions of refractories are obtained as well.

2.2 Setup to study corrosion problems under realistic conditions – TOM_chem

Besides the thermomechanical loads which are responsible for degradation of refractories by crack formation and growth in the material due to thermal stresses, also corrosion and abrasion are highly relevant for the service life of refractories. This statement even holds if the refractories are not in contact to melts like in steel or glass production. A flow of hot corrosive gases or vapours, sometimes loaded by powder particles, is present in many thermal processes. Sources can be the combustion products from fossil fuels or special processing gases required for chemical synthesis. As an example, formed refractory components composed of tabular alumina and fused mullite which were exposed to PbO- and S-vapors in an industrial furnace, have been analyzed by X-ray diffraction (XRD). This allows identifying the chemical processes and emerging corrosion products causing the various, apparently different damage zones visible in Fig. 5. The predominant chemical compounds identified at the numbered spots are listed in Tab. 1.

Tab. 1 Chemical analysis of corroded refractory components shown in Fig. 5.

Pos.	Phase Composition	Al_2O_3 [mass-%]	SiO_2 [mass-%]	PbO [mass-%]	SO_3 [mass-%]	Status
1	$PbO \cdot PbSO_4$	0,11	0,07	87,8	11,3	Surface covering
2	$PbO \cdot PbSO_4$, $2PbO \cdot PbSO_4$	0,21	0,06	89,1	9,9	
3	glass, $2PbO \cdot PbSO_4$, $4PbO \cdot PbSO_4$, Al_2O_3	47,3	7,0	42,4	2,5	Corrosion with flaking; partially glass formation
4	Al_2O_3, α-,β-$2PbO \cdot PbSO_4$, SiO_2, glass	–	–	–	–	
5	Al_2O_3, $4PbO \cdot PbSO_4$, SiO_2, $Pb_{11}Si_3O_{17}$, glass	46,6	9,9	41,4	0,83	Corroded, porous
6	Al_2O_3, glass	52,0	12,5	34,3	0,08	

From the results it is now possible to make suggestions how to avoid or strongly reduce the susceptibility for this special kind of corrosion. Laboratory equipment which helps to optimize the material selection for industrial high temperature plants is highly desired. For that, a laboratory-scale device must allow testing the material stability against corrosion and abrasion under realistic conditions comparable to those in the pertinent industrial plant. Several options to conduct investigations in this field are currently available commercially. Options are ranging from small furnaces suited for ther-

Fig. 6 Photo of vacuum system of the TOM_chem setup

mal treatment in water vapour or other controlled atmospheres, over the well-known burner rig tests addressing the conditions in gas turbines (see, e.g. [15]), to testing of refractories' CO- or alkaline resistance or their acid solubility.

The new TOM_chem device at the Fraunhofer HTL has been designed to extend the testing capabilities beyond the above briefly mentioned techniques. It will provide a wide variety of gases and vapours, optionally loaded by powder particles, at controlled temperatures and flow velocities. As well, it will include a setup to measure weight changes of the samples during the exposure time. In more detail: gases like CO, CO_2, O_2, N_2, Ar, NH_3, SO_2, H_2O, H_2S, NO_x, C_xH_y, Cl and pressurized air will be available at flow velocities up to 40 m/s and temperatures up to 1450 °C. Alternatively, combustion gases from an industrial gas burner can be used. Optionally, vapours are produced in a separate furnace and added to the gas flow. For the study of abrasion phenomena, powders with particle sizes from 0,5 µm to 100 µm can be injected into the gas flow up to a content of 10 g/Nm^3. The sample weight during thermal treatment can be measured at any time by help of a magnetic suspension balance. As the gas flow would disturb the weighing, the flow is passed through a parallel channel for the time of weight determination. This parallel channel is also used to monitor the current gas composition. Fig. 6 shows the vacuum system of TOM_chem.

3 Final remarks

Further improvement in the reliability of service life prediction of refractories remains a challenge, which will rely on progress both in the theoretical understanding of damage processes and in the techniques available for experimental analysis of thermomechanical and chemical loads. Significant efforts to promote the state of the art are made in both fields of current research. In this paper is reported progress on the experimental side, introducing two new thermo-optical measuring devices suited to provide data about thermal shock and corrosion behaviour which were not available in the past. The results of these measurements under realistic, close-to-industry conditions are also expected to have a positive impact on model-based lifetime prognoses of refractory components. Pertinent work on these topics is under progress at Fraunhofer HTL in the framework of the project EnerTHERM [16].

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