New Perspectives for Investigating the Softening Behaviour of Refractory Products at High Temperature

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Almost regardless of their application, refractory products have to sustain high temperatures and substantial loads. Refractory products are subjected to mechanical loading at high temperature, for instance the weight of the refractory structure itself or ferrostatic pressure for steel or pig iron containing vessels. Even if not leading to the immediate collapse of the refractory structure, significant deformation can occur in refractory products under the combined effect of high temperatures and mechanical loadings, impeding the proper functioning of industrial equipment relying on refractories.

Thanks to an innovative testing equipment, the standard testing conditions (EN ISO 1893: Determination of refractoriness under load and EN 993-9: Determination of creep in compression), i.e. with different atmospheres and higher loading, and the knowledge about creep behaviour of refractory products was broadend. The primary creep stage of refractory products and the resulting microstructure are clearly impacted by the testing conditions, such as temperature, load or atmosphere, and in turn influence the creep behaviour in the quasi steady state. An optical dilatometer provides novel information about the two-dimensional behaviour of refractory products subject to increasing temperature and loading. Such data can be decisive to support the development of 3-dimensional models to better understand, or even optimise, the behaviour of complex refractory structures.

1 Introduction

Even before considering the resistance of a refractory product to corrosion or to thermal shock, its capacity to withstand the process temperature without collapsing mid- to long-term decides whether it is suitable for a specific application. Cordierite refractory products are considered as a textbook example: They show high thermal shock resistance, but start softening above 1200 °C, therefore limiting their application mainly to kiln furniture with a maximal service temperature of approximately 1350 °C [1]. First and foremost, the combined effect of temperature and load is decisive at operating temperature. Individual parts of typical refractory structures support the weight of the parts, which are above them. For instance, in a refractory brick-work (wall, crown), the bricks in the lower parts support the weight of all the bricks above them. The load can in addition originate from a solid or liquid product, which is contained in a refractory structure, for example the ferrostatic pressure of the molten steel bath in vessels for steel production. Although these loadings remain relatively low, especially compared to the crushing resistance of refractory products, the high temperatures promote their deformation nonetheless.

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The softening behaviour of refractory products is typically assessed using standardised conditions, set up in EN testing standards. Though useful for comparison purposes, these standardised testing conditions allow only a limited insight in the softening behaviour of refractory products and merely consider the deformation (mostly compression) in one direction. For better assessment of the behaviour of refractory products under load, it is however important to consider variations in the testing conditions and introduce a novel method to assess two dimensional deformation.

2 Fundamental considerations

Refractory products are usually heterogeneous coarse inorganic materials, which, when compared to monophase materials, display a melting range of up to a few hundred degrees centigrade. In practice, a gradual softening of the refractory product at high temperatures occurs instead of melting at a discrete melting point. Especially impurities in the matrix of refractory products lead to the formation of compounds with relatively low melting temperature, which form a viscous phase at refractory operating temperatures. Besides the arrangement and formation of crystal grains in the refractory, the amount of viscous phase and its distribution, mainly conditioned by its capacity to wet the grains as well as its rheological properties (viscosity), govern the softening behaviour of refractory products [2]. The observed softening of refractory products exposed to load at high temperature leads to permanent deformations, called creep. These permanent deformations basically depend on the load intensity and duration, exposure temperature and the microstructure of the considered material.

Since typical service conditions for refractory products imply high temperatures, their softening behaviour plays a significant role and limits their maximum operating temperature. Furthermore, for plants and furnaces where refractory linings must ensure and endure long operating time, deformations of the structure due to creep processes, e.g. the subsidence of refractories across a blast furnace stove, may hinder the proper operation (e.g. constriction of the air passages) with accompanying loss of process efficiency [3]. The assessment and understanding of the creep behaviour is therefore a crucial tool for refractory engineering, either for the material selection for a specific application or as a target for material development.

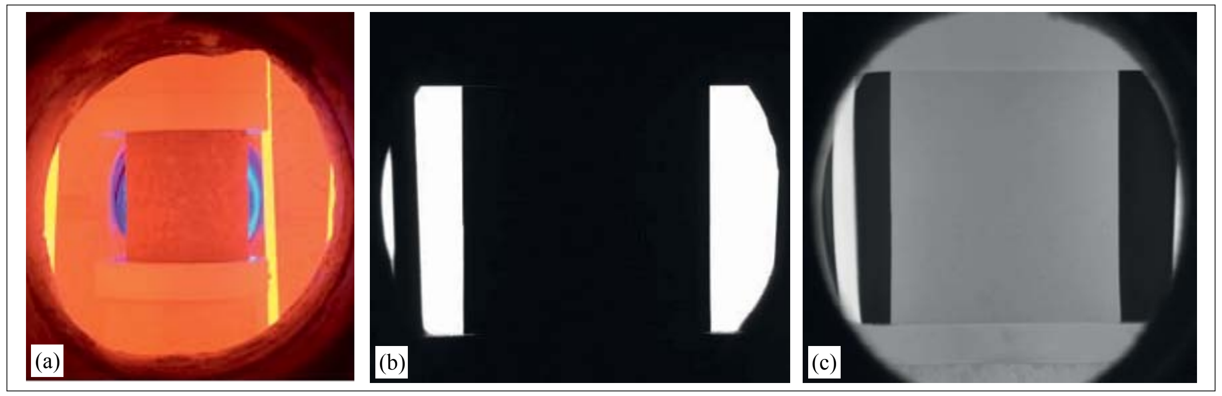

Fig. 1 36 mm × 36 mm refractory sample in the centre of the innovative testing equipment (a) at 700 °C. Images of the CMOS camera (optical dilatometer) (b) at room temperature (shadow of the sample), and (c) at 1500 °C (radiation of the sample)

3 Testing standards for measurement of softening behaviour of refractory products

The softening behaviour of refractory products is traditionally assessed using the testing standards EN ISO 1893: Determination of refractoriness under load, and EN 993-9: Determination of creep in compression or its U.S. equivalent ASTM C832 – 00: Method of Measuring Thermal Expansion and Creep of Refractories under Load. Both EN testing standards are carried out with the same testing equipment and similar testing procedures. A cylindrical refractory sample is subjected to a constant load (0,2 MPa) while increasing the temperature (5 °C·min^{-1}) in air. The deformation (height) of the sample is recorded continuously, usually with the differential method. For the determination of refractoriness under load (RuL), the test is stopped once a prescribed deformation is attained, typically 5 % of its initial length. For the determination of creep in compression (CiC), once a specified temperature has been reached, the temperature is maintained constant for a given time. The deformation of the sample at this constant temperature over time is then recorded. In both tests, temperatures corresponding to a characteristic degree of deformation are identified from the deformation against temperature/time curves.

4 Innovative testing equipment

The implementation of EN testing standards for the investigation of the softening behaviour of refractory products imposes very restrictive testing conditions. These clearly defined testing conditions are, on the one hand, essentially for the measurement of comparable values to be integrated in product data sheets. On the other hand they do not allow a comprehensive investigation and understanding of the behaviour of refractory products in use. In order to impose varying testing conditions, an experimental furnace for creep testing equipped with a high-load press and a system to control the atmosphere was developed. Measurements under oxidizing or inert atmosphere and with different loads can be performed to assess the high-temperature softening behaviour of refractory products.

A second decisive feature of this innovative testing equipment relies on the implementation of an optical dilatometer [4] in addition to the differential method to follow the deformation of the sample (Fig. 1). With such an optical dilatometer, the deformation of a sample can be accurately monitored while applying a load onto the sample up to high temperature. Compared to the differential method, the optical dilatometer additionally allows the recording of horizontal deformation. Such diversified deformation profiles can only be assessed with an optical dilatometer. The possibilities to adjust the testing condition to be closer to the service condition or simply vary testing parameters offer new insights for the investigation of the softening behaviour of refractory products. In addition, the two dimensional measurement of the sample deformations, thanks to the optical dilatometer, opens up new prospects for materials characterization.

5 Influence of atmosphere and loading on the softening behaviour of a commercial SiC containing refractory vibrating castable

Thanks to their intrinsic properties, SiC containing refractory castables have a large scope of application and hence are subjected to different operating conditions. Accordingly, different compositions and bonding systems have been developed. However, even for a specific application, a single com-

Tab. 1 Chemical analysis of the SiC containing castable under investigation

Component	Al_2O_3	SiO_2	CaO	SiC	Fe_2O_3
[mass-%]	48	25	2,5	20	<1,0

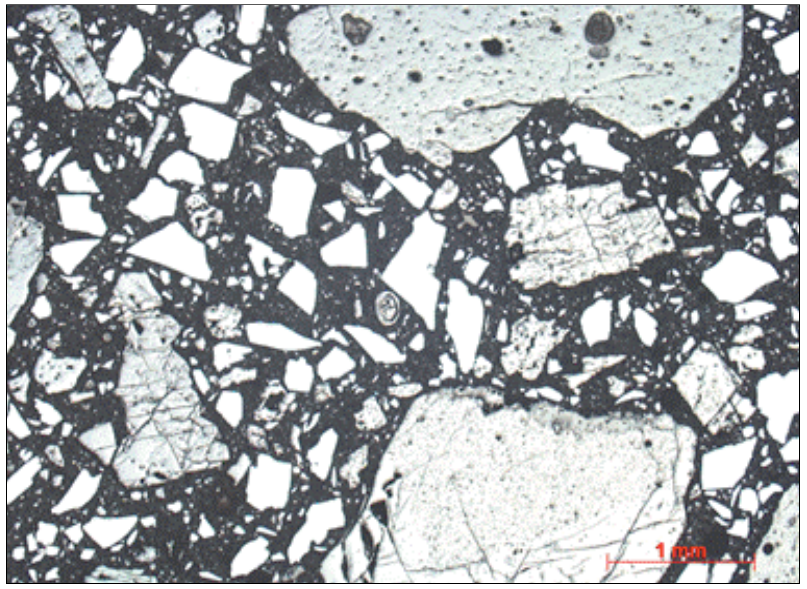

Fig. 2 Microstructural observation of the SiC containing castable after drying

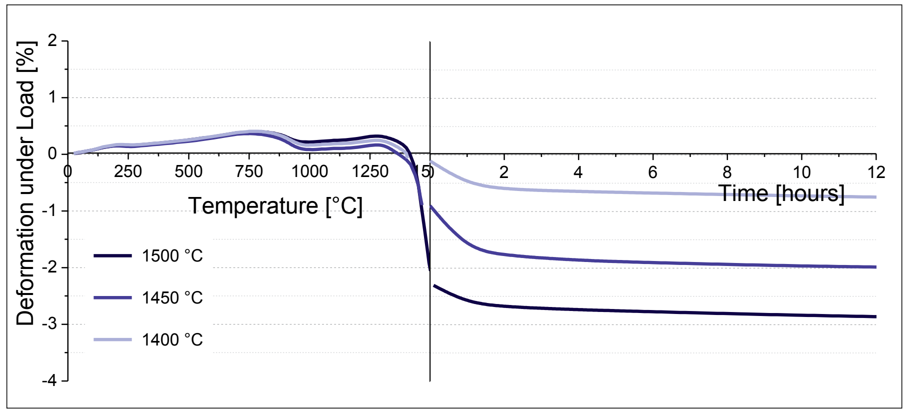

Fig. 3 Creep in compression measurements of the SiC containing castable at 1400 °C, 1450 °C, and 1500 °C in oxidizing atmosphere

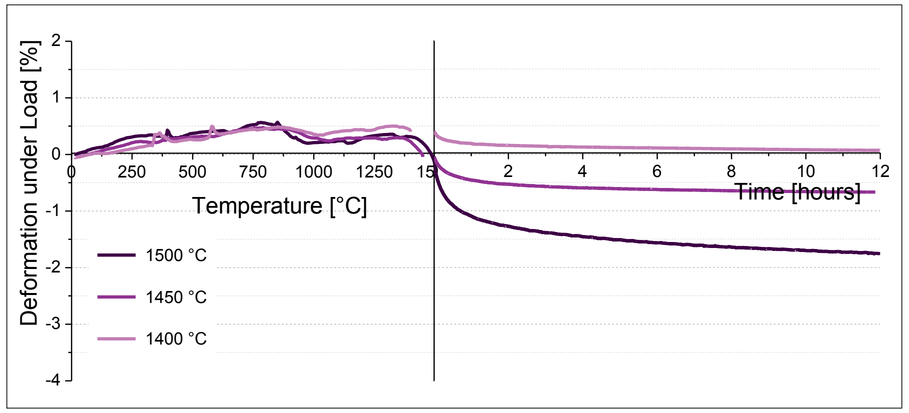

Fig. 4 Creep in compression measurements of the SiC containing castable at 1400 °C, 1450 °C, and 1500 °C in inert atmosphere

position can experience varying operating conditions. For instance in thermal process equipment, the atmosphere may vary from oxidizing to very low partial oxygen pressure and even reducing in a single process cycle. Thereby the innovative testing equipment was found to be particularly suitable for a sound and extensive characterization of the creep behaviour of SiC containing refractory castables.

Tab. 1 shows the chemical analysis of a commercial SiC containing refractory vibrating castable. According to XRD and microstructural observations (Fig. 2), cast samples are mainly composed of coarse grains of andalusite, along smaller grains of silicon carbide and a matrix with fine grains of corundum, synthetic mullite, quartz and cristobalite. For the investigation of the creep behaviour of this material, 36 mm × 36 mm cylinders were prepared by drilling and cutting unfired cast samples.

Creep tests under constant load (0,2 MPa) were performed at different temperatures for both oxidizing (air) and inert (Ar) atmospheres (Fig. 3–4). The creep rates measured during these tests in quasi steady state after 12 h (quasi linear part of the curve) are given in Tab. 2. The deformation levels at the end of the primary creep regime (first hours; fast decrease of the sample height) increased with increasing testing temperature. Similarly, the creep rates in quasi steady state (after 12 h) increased with increasing testing temperature. However, for the same temperature and initial stress, the deformation levels at the end of the primary creep regime were found to be significantly more pronounced in oxidizing atmosphere compared to inert atmosphere. Microstructural observations showed that a more intensive densification was achieved in oxidizing atmosphere (Fig. 5).

At least up to 1450 °C, the creep rates in quasi steady state (after 12 h) were found to be lower in inert atmosphere compared to oxidizing atmosphere. Nevertheless, at 1500 °C this reversed and the creep rate of the samples after 12 h in inert atmosphere became strikingly higher compared to those of the samples in oxidizing atmosphere (Tab. 2).

The impact of the initial stress on the deformation level at the end of the primary creep regime (first hours) was examined and found to be unsurprising and unequivocal: The higher the initial stress, the higher the deformation level (Fig. 6). By contrast, the effect of the initial stress on the creep rate in quasi steady state (after 12 h) was found to be much less obvious (Tab. 3).

By preventing the passive oxidation of SiC and more generally the appearance of (more) viscous phases, the creep process appeared to be impeded in inert atmosphere. Up to 1450 °C, both deformation levels at the end of the primary creep regime and the creep rates in quasi steady state were found to be higher for measurements in oxidizing atmosphere (Fig. 3–4). At 1500 °C, the creep rate after 12 h in inert atmosphere clearly exceeded the creep rate in oxidizing atmosphere (Tab. 2). This was explained by the fact that, as soon as enough viscous phase had been formed, the much looser microstructure achieved during tests in inert atmosphere offered more potential for creep (Fig. 5). In comparison, the relatively denser microstructure obtained under oxidizing atmosphere seemed to hinder further creep progress, i.e. a lower creep rate in quasi steady state was achieved. The results from the investigation of the impact of initial stress (Fig. 6) tended to confirm this effect. Higher initial stress was expected to lead to a higher creep rate, but the high densification level attained in practice after the primary creep under high initial stress practically impeded further deformations. The creep rates in quasi steady state (after 12 h) did not show a clear dominant trend with increasing initial stress level (Tab. 3).

6 Investigation of two dimensional deformation

In addition to the (horizontal) deformation in the direction of the applied load, for the first time for the characterization of refractory products the vertical deformation has also been continuously monitored. Three different kind of refractory products were investigated that showed different behaviour.

6.1 Magnesia refractory product

Optical investigation of the deformation behaviour was carried out on a relatively homogeneous and rather simple magnesia refractory product (Tab. 4). Until roughly 1400 °C, an isotropic thermal expansion of the sample was observed. Above 1450 °C,

Tab. 2 Creep rate [%·h⁻¹] in quasi steady state ("secondary creep" after 12 h) for an initial stress of 0,2 MPa, different temperatures and different atmospheres

	1400 °C	1450 °C	1500 °C
Oxidizing atmosphere	0,0108	0,0121	0,0142
Inert atmosphere	0,0067	0,0083	0,0333

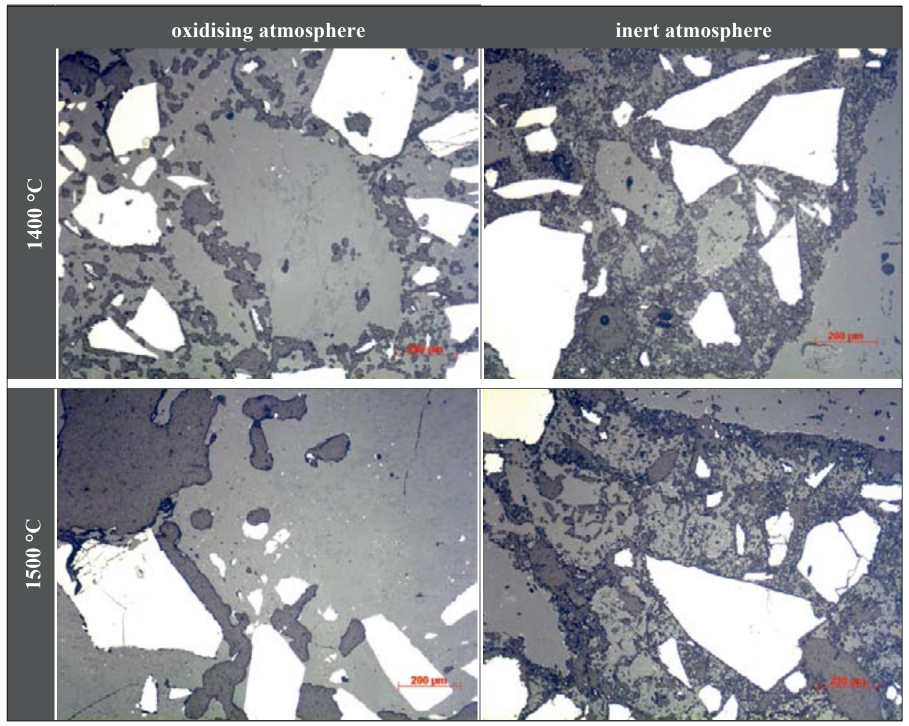

Fig. 5 Microstructural observation of the SiC containing castable after 12 h CiC measurements at different temperatures for oxidizing (air) and inert (Ar) atmosphere

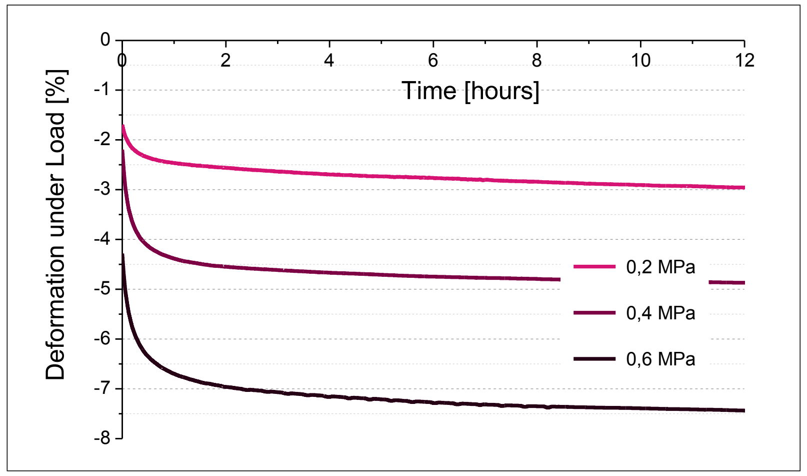

Fig. 6 Creep in compression measurement at 1500 °C in oxidizing atmosphere for three different initial stresses of 0,2 MPa, 0,4 MPa, and 0,6 MPa

Tab. 3 Creep rate [%·h⁻¹] in quasi steady state ("secondary creep") at 1500 °C in oxidizing atmosphere for three different initial stresses of 0,2 MPa, 0,4 MPa and 0,6 MPa

	0,2 MPa	0,4 MPa	0,6 MPa
Oxidizing atmosphere	0,016	0,009	0,012

Tab. 4 Chemical analysis of the magnesia refractory product

Component	Al_2O_3	SiO_2	CaO	MgO	Fe_2O_3	TiO_2	Na_2O	P_2O_5	K_2O
[mass-%]	0,34	1,61	1,31	95,87	0,66	0,02	0,01	0,09	0,03

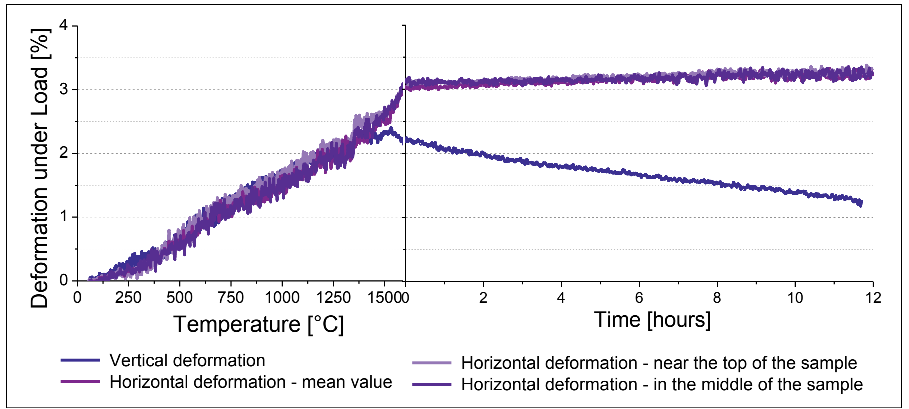

Fig. 7 Creep in compression measurement of the magnesia refractory product at 1600 °C in oxidizing atmosphere (testing condition as stated in the standard EN 993 – 9).

Tab. 5 Creep rate v after 12 h for an initial stress of 0,2 MPa and different temperatures in oxidizing atmosphere

Creep Rate v [%·h⁻¹)]	1500 °C	1600 °C
in the loading direction (subsidence)	0,048	0,068
perpendicular to the press direction (swelling)	0,003	0,008

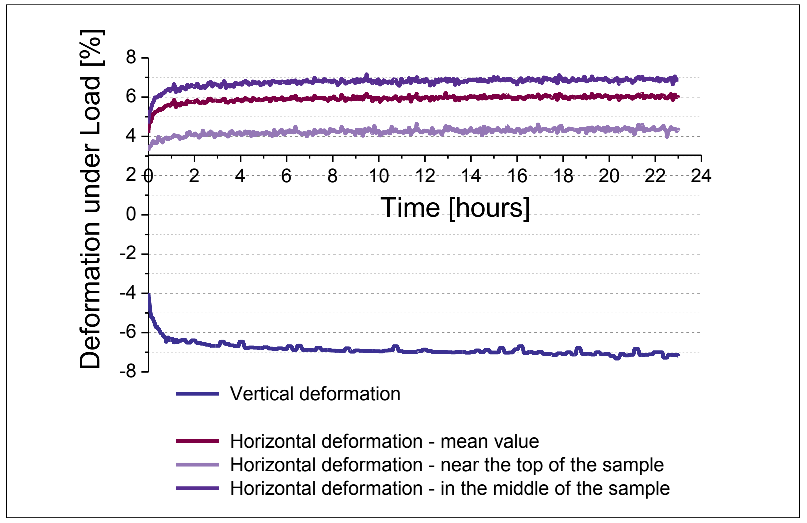

Fig. 8 Creep in compression measurement of the SiC containing refractory castable at 1500 °C in oxidizing atmosphere and an initial stress of 0,6 MPa

irreversible deformations were found to occur. The path of the curves (Fig. 7) showing horizontal and vertical deformations accordingly began to diverge significantly. Especially, once the desired dwell temperature was reached, the subsidence of the sample was clearly observed in the direction of loading (vertical). Despite the relatively high content of magnesium oxide in the reference sample, the amount of impurities in the matrix was suspected to be high enough to lead to the formation of eutectic compounds with low melting point (<1500 °C) at the grains boundaries, promoting the creep of the sample in the direction of the applied load.

The progressive melting of the eutectic compounds resulted in the formation of a viscous phase in the sample. Mainly the amount of this viscous phase and its distribution, basically conditioned by its capacity to wet the grains (contact angle) as well as its rheological properties (viscosity), were assumed to govern the creep behaviour of this magnesia refractory product.

In the direction perpendicular to the loading direction ("horizontal deformation"), a slight swelling of the sample was measured. In case of magnesia refractory products, this swelling was almost independent of the measurement position (top or middle of the sample).

An increase of temperature lead to a slight increase of the creep rates after 12 h (Tab. 5). The amount of viscous phase is expected to increase with higher temperature and the viscosity of the viscous phase decreases with temperature, promoting the deformation of the magnesia refractory sample under load.

6.2 SiC containing castable

Optical measurements were also performed on the SiC containing castable (see chapter 5). The horizontal deformation near to the top and the bottom of the cylindrical sample turned out, this time, to be significantly smaller than the deformations in the middle of the sample where the sample was free to expand (Fig. 7). These observations were in agreement with the visual examination of the samples, which took the typically barrel shape.

The creep rates of the SiC containing refractory castable in different directions and even at different positions were also assessed for the first time (Tab. 6). Even though measurements of small creep rates are difficult to assess with high reliability, the determined creep rates were found to be coherent with the physical evolution of the sample. The cylindrical samples showed a slight global swelling, more pronounced in the middle of the samples, so that the samples slowly tended to assume a barrel shape. Although already well known, this phenomenon could not be assessed and quantified during CiC measurements until now. Traditional studies and models focused on a one-dimensional approach of the creep process for refractory products, neglecting deformations in direction other than the press direction. At this point, the optical dilatometer of the innovative testing equipment provided new decisive information, especially to support the development of 3-dimensional models.

6.3 Alumina-Zirconia-Silica (AZS) refractory product

Widely used in the glass industry, fused-cast refractory material is the key refractory material in modern glass production. Exceptionally for refractory materials, the amount of the glassy phase in fused-cast Alumina-Zirconia-Silica (AZS) products is quite important and appreciable. The relatively high amount of glassy phase leads to a singular behaviour.

When testing the creep behaviour, the first noteworthy feature was the slowing of the thermal expansion and even a light shrinkage between 1050 °C and 1300 °C (Fig. 9), which is due to the polymorphic change of the ZrO_2 phase. Above 1300 °C, the AZS sample seemed to experience significant expansion or deformation according the optical measurements in the horizontal direction. In practice, promoted by the load applied on the sample, the glassy phase present in the products was progressively exuded. Firstly the exuded glassy phased was detected as a coating, the thickness of which increased with increasing temperature. At higher temperatures, even wetting of the sample supports occurred above 1600 °C (Fig. 10).

The temperature at which the glassy phase started to build a coating on the AZS sample and then began to wet the sample support could easily be determined with the optical dilatometer.

Tab. 6 Creep rates [%·h⁻¹] of SiC containing refractory castable in quasi steady state ("secondary creep") at 1500 °C in oxidizing atmosphere and an initial stress of 0,6 MPa

Optical Method			
Vertical Deformation (Loading Direction)	**Horizontal Deformation**		
	Mean value	Near to the top of the sample	In the middle of the sample
0,0125	0,0042	0,0038	0,0050

Tab. 7 Indicative composition of the tested alumina-zirconia-silica (AZS) refractory product

Component	Al_2O_3	ZrO_2	SiO_2
[mass-%]	51	32	15

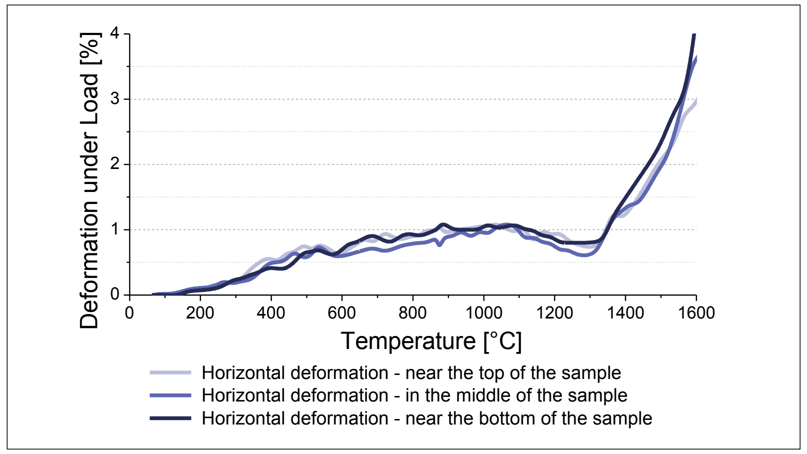

Fig. 9 Horizontal deformation measured at different positions during a refractoriness under load measurement of an AZS sample in oxidizing atmosphere (air), and an initial stress of 0,6 MPa

7 Conclusions

The softening behaviour of coarse refractory products at elevated temperature is a complex issue. Operating conditions such as temperature, load and atmosphere play a decisive role. Since the existing testing standards and equipment cannot mirror the operating conditions for industrial application of refractory products, the prediction of the softening behaviour of a refractory lining in service, based on measurements according to these existing testing standards, is to be used with extreme caution. Besides, refractory linings experience unsteady thermal gradients and pressure gradients in practice, an extensive investigation is therefore necessary for a good understanding and sound modelling of the refractory softening behaviour.

The use of innovative testing equipment with controlled atmosphere for creep testing is crucial in order to soundly characterise the softening behaviour of materials sensitive to oxidation such as SiC. An ex-

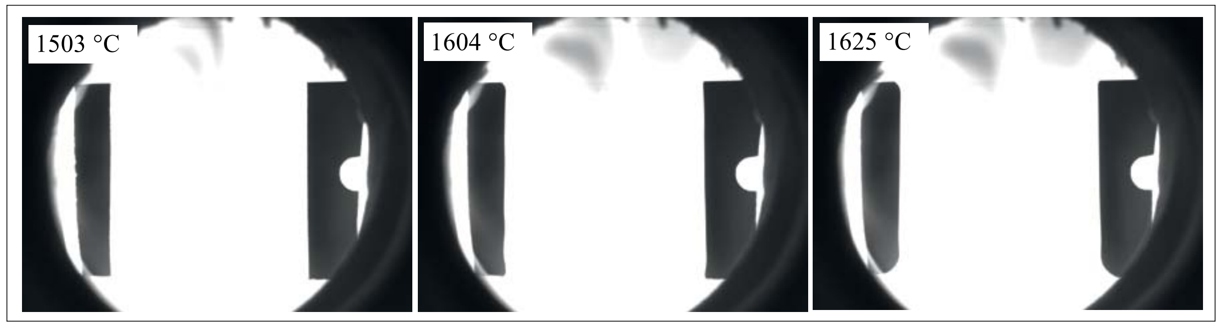

Fig. 10 Thermooptical measurements over the course of the refractoriness under load testing on an AZS sample in oxidizing atmosphere (air)

emplary study of the softening behaviour of SiC containing castable highlight the impact of the atmosphere in industrial equipment using SiC containing castables.

The optical dilatometer implemented in the innovative testing equipment provided insight and new information about the two-dimensional creep behaviour of refractory products. Three different refractory products (a magnesia refractory, a SiC containing castable and Alumina-Zirconia-Silica (AZS) refractory) displayed different and distinct behaviour which could not have been soundly investigated and quantified without 2-dimensional optical measurements. The information provided by the 2-dimensional optical measurements is new in the field of refractory characterization. Especially for the simulation of the behaviour of refractory linings in complex industrial systems, for which many spatial limitations exist, results from standard one-dimensional deformation measurements should only be used with care.

Information on the deformation in a second dimension, as provided by the optical dilatometer of the innovative testing equipment, is decisive for the development and validation of complex creep models and should greatly improve the accuracy of complex numerical simulations.

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