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Entwicklung von Testmethoden und Modellen zur Beschreibung des Erweichungsverhaltens feuerfester Werkstoffe („CreepRef“)

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Vorwort

Das IGF-Vorhaben 74 EN der Forschungsvereinigung Forschungsgemeinschaft Feuerfest e.V. wurde über die AiF im Rahmen des CORNET-Gesamtprojekts bewilligten IGF-Vorhabens (CORNET-Teilprojekt) vom Bundesministerium für Wirtschaft und Energie aufgrund eines Beschlusses des Deutschen Bundestages gefördert.

Der vorliegende Forschungsbericht ist auf Englisch verfasst und fasst die technischen Ergebnisse zusammen, die für das CORNET-Teilprojekt der AiF-Forschungsvereinigung Forschungsgemeinschaft Feuerfest e.V. erzielt wurde.

Am dem transnationalen CORNET-Gesamtprojekt war außerdem das Centre de Recherches de l'Industrie Belge de la Céramique (CRIBC) in Belgien beteiligt, gefördert durch Service Public de Wallonie (SPW).

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1. Scientific-technical and economical scope of work

1.1. Introduction

The main end use of refractory materials is lining of high temperature industrial facilities (furnaces, reactors, vessel...) in the sectors of iron and steel production (70 % of refractory materials used in this sector), cement production (7 %), chemicals (4 %), ceramic production (5 %), glass production (4 %) and production of non-ferrous metals (5 %).

During their service life, refractory materials (“refractories”) are subjected to various stresses. In most applications, the basic stresses are:

- Pressure: Individual parts of the refractory structure support the weight of the parts which are above them. For example, in a brickwork (wall, crown), the refractory bricks in the lower part of the brickwork support the weight of all the other bricks above them. The pressure can in addition be due to a solid or liquid product which is contained in a vessel; for example, in the bottom of a steelmaking ladle, the refractory lining support the weight of the liquid steel.
- Temperature: The exposure to high temperature is obvious. Refractory materials can be subjected to temperatures as high as 1850 °C.

The pressure on refractories is generally relatively low, far below the crushing strength. However, elevated temperature promotes the deformation of refractories. The result of the simultaneous effect of pressure and high temperature can be a significant creep (deformation, in function of time, under constant load) of refractory materials. This phenomenon can further be intensified by contamination of the refractory materials during their service life.

Nowadays, many high temperature industrial facilities are still designed by taking into account the “recommended maximum use temperature”, the density, the porosity and the mechanical properties (mainly the resistance to compression, but also the bending strength, the modulus of elasticity) of refractory materials at *low temperature*. Only a very limited number of properties are also measured at *high temperature*: modulus of elasticity, bending strength, thermal conductivity and linear thermal expansion.

Some parameters, such as thermal conductivity, elastic modulus and thermal expansion coefficient allow simulating the thermal exchange and the mechanical stress at high temperature. For example, thermal expansion coefficient is currently used to determine the distance between expansion joints and to avoid excessive stress in the lining. **However the creep is generally neglected.**

1.2. General description of the problem

Users of refractory materials are currently concerned with the need to improve the profitability and the reliability of their industrial facilities. Their wishes are mainly:

- › to increase the service life,

- › to avoid any disturbance in service,
- › to avoid unpredictable shut down of production,
- › to plan stopping and maintenance events well in advance,
- › to operate with a high flexibility in terms of energy source (kind of combustible and oxygen), parameters of the process and composition of the production,
- › to control environmental and safety aspects,
- › to understand the effect of operating parameters in the production.

All these require characterising, modelling and predicting of the behaviour and the ageing of the facilities. This needs a good knowledge of the high temperature behaviour of the refractory materials used for lining those facilities and especially their evolution over time (creep).

A number of publications deal with theoretical aspects of creep of ceramic materials. Literature also proposes some information concerning the behaviour of refractory materials under stress at high temperature. Only very little creep data for industrial refractory materials is published from experiments where the refractory materials were tested in conditions near to the real conditions that affect the refractory materials in industrial use.

Generally, refractory suppliers provide very limited data concerning the high temperature behaviour of their products and hardly communicate any information concerning creep in their data sheets.

In laboratories, creep is measured according to a standard method. In Europe, the ISO and EN standards specify to use one constant load (0.2 MPa) and measure the subsidence of the sample in the loading direction. The measurements are typically performed in ambient air (oxidising atmosphere). The testing conditions of the refractories are thus generally not compatible to the real conditions in industrial use and the results are therefore not considered sufficient to predict the evolution in function of time in service. Although measurements in ambient air are quite easy to perform, they are not representative of service conditions for refractory products. Refractory linings in contact with molten metals as well as linings in combustion plants and waste incinerators typically work in atmosphere with low oxygen partial pressure. Many modern high-tech refractory products, such as carbon bonded refractory products, are even sensitive to oxidization. An inert atmosphere, to prevent burning off the carbon fraction, is thus crucial for the testing of such carbon bonded refractory products.

Experimental data describing the high-temperature behaviour of refractories in real conditions is also of great value for computational methods for simulating the behaviour of refractory materials at high temperature. The current characterisation tools have to be improved and new methods of investigation have to be developed.

1.3. Innovation targets

It is obvious that, in a near future, an increasing number of users will require information concerning the high temperature behaviour of refractory materials and especially about creep behaviour.

Moreover knowledge of creep is more complex than “measuring deformation versus time under load at high temperature”. Investigation about the creep of refractory materials is very critical for different reasons:

- There is a wide range of refractory materials,
- There is a wide range of raw materials to produce refractory materials,
- the introduction of new raw materials (recycled products for example),
- the discontinuous behaviour of refractories in function of temperature (appearance of liquid phase, phase change...),
- the change of the chemical composition of refractories, in function of time, due to contamination in use,
- the change of the crystallographic composition in function of time,
- the change of the microstructure after exposure for a long time at high temperature.

It was thus necessary to carry out activities in the field of creep measurement and characterisation as well as in the field of understanding the creep behaviour of refractory materials.

The main objectives of the project were:

- to **improve characterisation tools** in order to extend the conditions recommended in the standards, for example, to enlarge the range of pressure. Basically providing a better insight into the products behaviour, it would in addition enable to achieve a sound modelling and verify models. Hereby, measurements under only one testing condition are completely insufficient. A further necessary improvement lies in the control of the testing atmosphere to enable, for instance, oxygen sensitive products to be properly characterized or to investigate the impact of atmosphere on the high temperature behaviour of a given refractory product.
- to **develop new methods of investigating** for the assessment of the creep behaviour of refractory products. Along with the measurement of the subsidence of the sample in the pressing direction (vertical), the acquisition of the horizontal deformations of the sample represents a decisive step forward. Once again, in addition to improve understanding of the refractory product creep behaviour, the horizontal deformations of the sample constitute to a new set of information to be included in the modelling of the creep behaviour for refractory products. Clearly enhanced modelling and predictions can be achieved.
- to **improve and/or develop model(s)** for the characterisation of the creep behaviour of refractory products. The knowledge of creep of materials is of high interest, because it is necessary to estimate the service life of the industrial structure and to ensure their integrity during a sufficient time. Finally, it is necessary to establish a correlation between the results of creep measurement and the other characteristics of the products.

Within the framework of the CORNET project collaboration, Forschungsgemeinschaft Feuerfest e.V. (Germany) worked on the two first objectives, while Centre de Recherches de l'Industrie Belge de la Céramique (Belgium) was mainly responsible for the third one.

Eventually, the knowledge developed during the project lead to advices for modification of materials characteristics with the purpose of controlling or improving their resistance to creep deformation.

2. Description of the technological developments envisaged in the project

2.1. State-of-the-art and technological alternatives

2.1.1. Refractory products and their creep behaviour at high temperature

Refractory products

Refractory products are ceramic materials (inorganic and non metallic materials)

From their chemical composition, refractory materials can be classified as:

- alumina-silica family with includes silica products ($\text{SiO}_2 > 93 \%$), fireclay (Al_2O_3 ranging from about 20 to 45 %) and high alumina products (Al_2O_3 ranging from about 60 to more than 95 %)
- basic products mainly based on magnesia (MgO) and doloma (MgOCaO)
- special products including oxides such as zircon (ZrSiO_4) and non-oxides such as silicon nitride (Si_3N_4), silicon carbide (SiC) and carbon (C).

Carbon and/or silicon carbon (SiC) can be also added to oxide materials to improve their resistance to corrosion.

The range of raw materials is very large: they are natural (clays, zircon sand, quartz,...) or synthetic (alumina, silicon carbide,...). Nowadays, recycling products are more and more used.

There are several main ways to manufacture or install refractory materials. The most current method consists of pressing or ramming a mixture of granular raw materials in a mould to obtain shaped products and to heat them at high temperature to achieve the ceramic bonding. The second most popular method consists of casting a slurry of raw granular materials (unshaped product) with water to obtain a monolithic product. This step is generally realised on site and the ceramic bonding is obtained during the first heating in service.

Refractory materials are made of fine and coarse particles (figure 1). The coarse particles or aggregates exhibit a grain size higher than about 0,1 mm and up to several millimetres. Due to their large size, their small surface on volume ratio, they are the most inert (thermally and chemically) part of the material. They also form the network of the structure. Fine particles are generally considered as the bonding phase or matrix of the material. Due to their large surface area, these fine particles are more reactive. At high temperature, during the heating, they sinter and lead to a ceramic bonding between the aggregates.

The bonding phase is generally different from the aggregates. The chemical composition can be different, it contains more impurities which lead to a lower refractoriness (resistance to temperature). Generally the porosity of the bonding phase is higher than the porosity of aggregates leading to a lower resistance to corrosion.

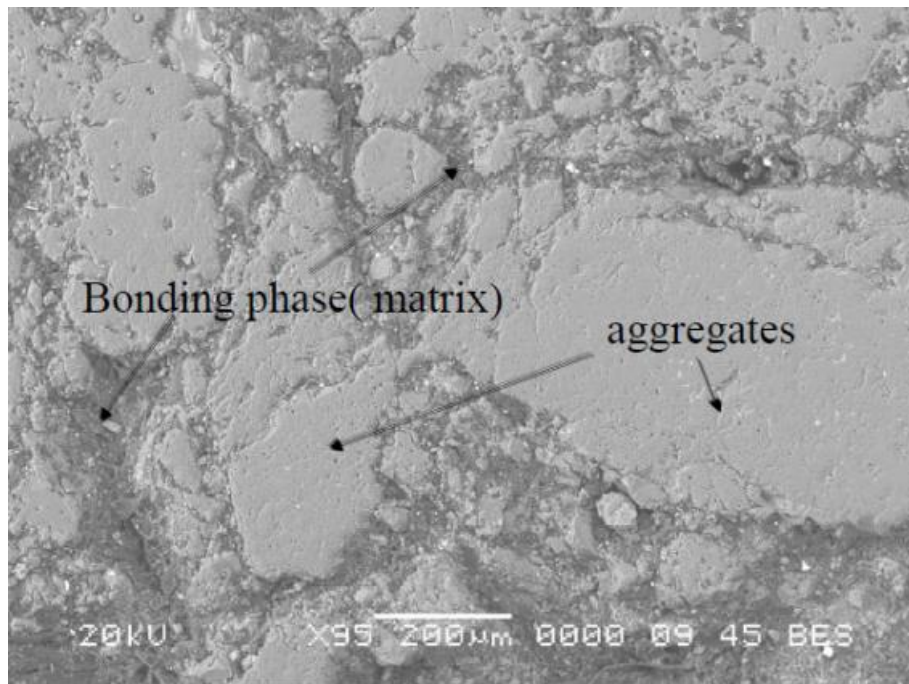


Fig. 1: Typical microstructure of a refractory material.

In the case of monolithic materials, the cohesion at low temperature can be due to a hydraulic cement: calcium aluminate which introduces calcium in the composition and thus decreases the refractoriness.

The ratio between the bonding phase and the aggregates are generally calculated to obtain products as dense as possible. For castables, compared to pressed product, a very high proportion of fine particles is used to promote a low viscosity and a good flowability with a minimum of water.

Another kind of refractory materials which are used at very high temperature in glass furnace are the electrofused (electrocast) materials. The manufacture process is similar of that one of cast iron. The composition is melted in an electric furnace and the melt is cast in a mould. During cooling, some crystallographic phases appear but an amorphous phase remains between the grains.

Creep behaviour of refractory products at high temperature

Creep is the permanent deformation of a material, versus time, under a constant stress.

The rate of deformation is a function of the material, time, temperature and applied stress.

The creep curves plot the increase of strain ϵ versus time t (at constant stress). The most classical curve, usually observed for metals and sometime for oxides, shows three stages with different slopes:

- a primary step (I) in which the creep rate decreases with time,
- a secondary steady state step (II) with a constant strain rate,
- a tertiary stage (III) in which the strain rate increases continuously up to the fracture.

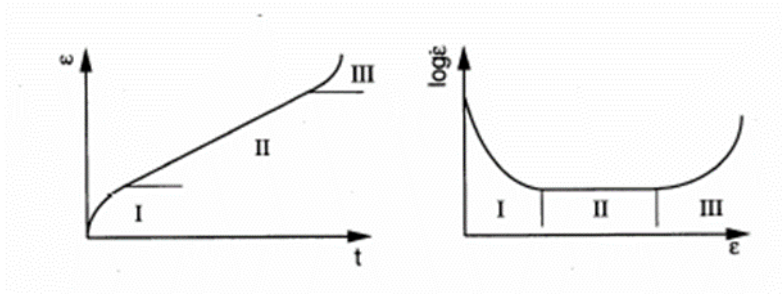


Fig. 2: Exemplary creep curve.

The number of stage and the shape of the curves may differ but the steady state is always present.

Materials can be characterised by their steady state creep, which can be described through the following relation:

$$\dot{\varepsilon} = A D G \frac{b}{k T} \left(\frac{b}{d}\right)^p \left(\frac{\sigma}{G}\right)^n \quad (1)$$

where : $\dot{\varepsilon}$ is the creep rate, D is the diffusion coefficient, G is the shear modulus, b is the Burger's vector, k is the Boltzman's constant, T is the absolute temperature, d is the grain size, n is the stress exponent, A is a dimensionless constant, σ is the stress, p is the exponent of the inverse grain size. The diffusion coefficient, D is thermally activated and given by:

$$D = D_0 \cdot \exp\left(-\frac{Q}{R \cdot T}\right) \quad (2)$$

where: D_0 is a frequency factor, Q is the activation energy, R is the perfect gas constant.

Creep can be also described through a simplified equation on the form of Norton-Bailey-Arrhénus relation:

$$\dot{\varepsilon} = A \cdot \sigma^n \cdot \exp\left(-\frac{Q}{R \cdot T}\right) \quad (3)$$

where: $\dot{\varepsilon}$ is the creep rate, A is a dimensionless constant, σ is the stress, n is the stress exponent, Q is the activation energy, R is the perfect gas constant, T is the absolute temperature.

The mechanical properties of the refractory products depend to a large extend of the bonding phase. The creep behaviour is no exception to this. The high temperature characteristics and the creep behaviour of the refractory materials can be generally related to the presence of vitreous-viscous phases and/or appearance of liquid phases at the grain boundary at high temperature. When compared to monophasic material, the typically heterogeneous refractory products display a melting range of up to a few hundred degrees centigrade, meaning a gradual softening of the refractory product at high temperatures instead of melting at a discrete melting point. Especially impurities in the matrix lead to the formation of compounds with relatively low melting temperature which form a viscous phase at refractory operating temperature. This means that the high temperature behaviour of refractory material is very

sensitive to the composition and particularly to the presence of silicates and “impurities” (alkali and alkali-earth oxides). Beside 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 grain as well as its rheological properties (viscosity), are assumed to govern the creep behaviour of refractory products [1].

2.1.2. Standard testing equipment for refractory creep measurement

The measurement of creep consists of measuring the height variation of a sample under load versus time, in a furnace at high temperature.

Several methods are being described in the literature. The load can be applied through calibrated weights or with a press. In some devices, the weight is the furnace itself and the load is regulated with a counterweight (Fig. 3). The height variation of the sample is generally followed with an extensometer or with a differential method. The differential method (Fig. 4) consists of measuring the distance between the lower and the upper face of a sample. The extensometer consists of two probes in contact with the sample surface at different height and the measure is the variation of the distance between the probes extremities (Fig. 5). The measurements are realised with a capacitor sensor or a linear variable differential transducer.



Fig. 3: Creep equipment where the applied load is the furnace itself and is regulated with a counterweight (source: Netzsch).

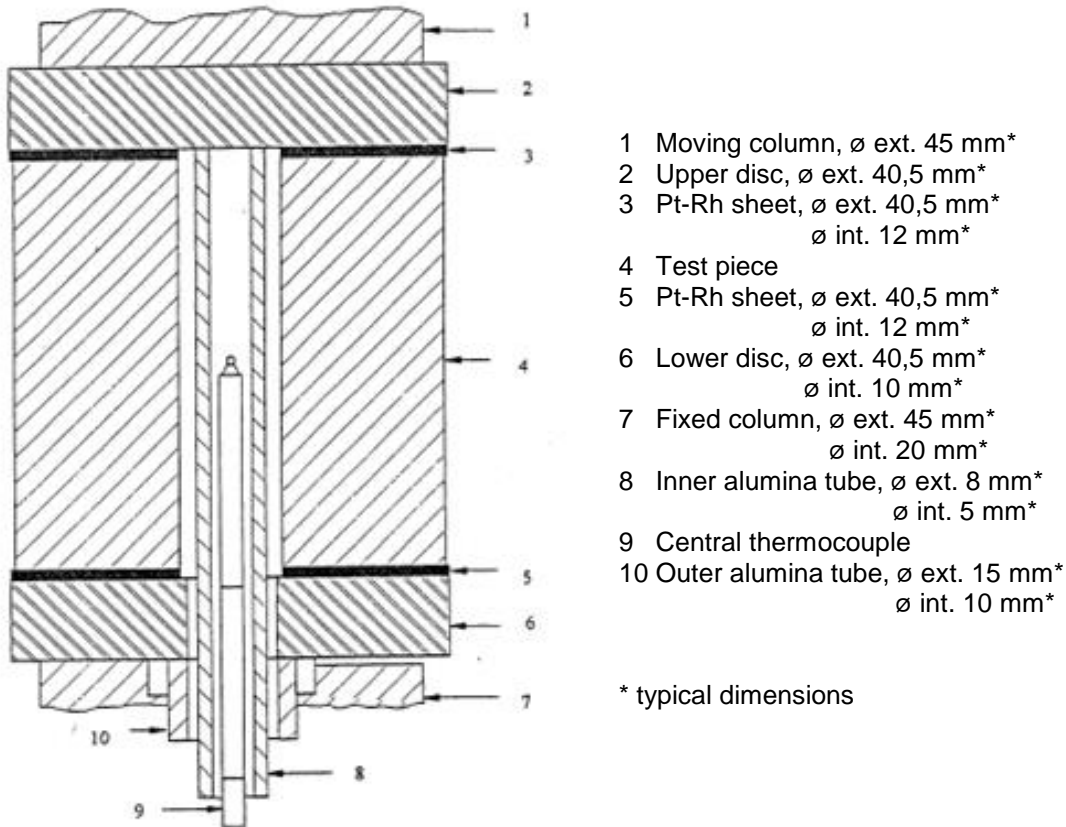


Fig. 4: Differential method allowing the measurement of the distance between the lower and the upper face of a sample.

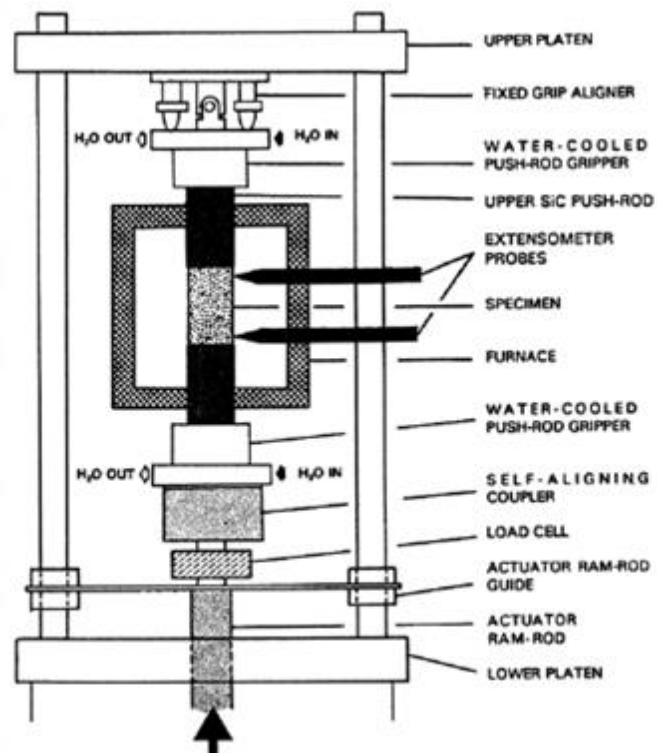


Fig. 5: Method to measure the creep with a mechanical extensometer.

The US testing standard ASTM (C832-89) [1] describes three possible devices: absolute height measurement of the sample and calibration of the device, use of an extensometer or use of a differential method. The standard recommends using 0,172 MPa of load, but other stress level may be used.

In Europe, the creep behaviour of refractory products is basically assessed using the testing standards EN ISO 1893: Determination of refractoriness under load, and EN 993 - 9: Determination of creep in compression. Both testing standards are carried out with the same testing equipment and similar testing procedure. A cylindrical refractory sample is subjected to a constant load (0,2 MPa) while increasing the temperature ($5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) 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 [3]. For the determination of creep in compression (CiC), once a specified temperature of the sample 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.

2.1.3. Experimental testing equipment for refractory testing at high temperature and controlled atmosphere

Mechanical characterisation of refractory products up to the operating temperature of refractory linings and under service conditions is a challenging issue. Thereby, the testing equipment should not only be able to reach temperatures above $1500\text{ }^{\circ}\text{C}$, but should be able to work under different kind of atmospheres. In order to achieve this, FGF has been developing an experimental testing device in recent years. The basis of the experimental testing device is an autoclave furnace, which is equipped with an optical dilatometer and a press to apply load (Fig. 6). For application at high temperatures, the load from the press is transmitted to the sample with a moving column made of alumina (Al_2O_3).

A system to control the atmosphere in the autoclave furnace allows testing oxygen sensitive materials such as carbon containing refractory materials in a reliable way. The autoclave furnace is connected to a vacuum pump for evacuation and, once a sufficient vacuum is achieved, the autoclave furnace can be filled with a technical gas, such as argon, nitrogen or a gas mixture. The gas flow rate itself is controlled with a ball float types flowmeters for flow rates from 0 to 500 NI/h (calibrated for Nitrogen 1 bar above $20\text{ }^{\circ}\text{C}$). For flow rates below 80 NI/h and precise gas mixtures, two thermal mass flow meters are also available.



Fig. 6: Experimental testing device, showing the autoclave furnace equipped with a press and a system to control the atmosphere.

2.2. Research method

The research was carried out in three consecutive steps.

Firstly, the experimental testing device, available at FGF, was upgraded to achieve an enhanced characterisation of the creep behaviour of refractory products according to the objectives of the research project. In the course of this development, a module to use the differential method as described in the ASTM standard and recommended in the ISO and CEN standards was designed and implemented at the experimental testing device. Measurement results for creep behaviour obtained with the upgraded experimental testing device were compared with results obtained with classical standard testing systems on reference materials in order to verify the proficiency of the upgraded experimental testing device. Also, the atmospheric control system was considerably developed. The technological development is described in chapter 3.1.

Secondly, based on the optical dilatometer present in the experimental testing device, a further, new method for optical investigation of the creep behaviour of refractory products by evaluation of the optical observation of a sample during creep testing was developed. With the aid of the optical dilatometer of the experimental testing device, the two dimensional evolution of the sample during creep testing was observed in real time for the first time. Once again, measurement results obtained with the optical dilatometer of the experimental testing

device were compared with results obtained with classical testing systems as well as with simultaneous measurements of the recently integrated differential method in the experimental testing device. The technological development is described in chapter 3.2.

Thirdly, extended conditions, such as the combination of higher loading, high temperature and inert atmosphere, were applied to investigate the creep behaviour of oxygen sensitive refractory products using the upgraded experimental testing device: one magnesia-carbon refractory product (MgO-C) and one SiC-containing unshaped refractory product (castable). Experimental results from the upgraded experimental testing device at high temperature in inert atmosphere were compared to experimental results from conventional high temperature testing apparatus, where possible, and they were correlated to characteristics of refractory products as well as microstructural observations. New insights in the creep behaviour of the investigated refractory products were gained and lead to the development of a phenomenological model describing the creep behaviour of refractory products. The technological development is described in chapter 3.3.

3. Technological development

3.1. Experimental testing device

3.1.1. *Upgrading the experimental testing device*

In this project, the testing conditions specified in the standards EN ISO 1893 and EN 993 – 9 were extended, especially thanks to the use of the experimental testing device:

- A specific module for measuring the height variation of the sample by means of the differential method was developed and installed. Hence, determination of refractoriness under load and determination of creep in compression measurements according to the standards EN ISO 1893 and EN 993 - 9 can be performed with the experimental testing device.
- In order to applied loading of up to 0,6 MPa at temperature corresponding to the typical service conditions of refractory products, in inert atmosphere, different specific improvements were implemented during the project. Most prominently, the upper moving column of the press, used to apply the load onto the sample, was enlarged. Although able to sustain the different loads used during the investigation, the initial alumina column tended to creep at high temperature. A new more massive column with high resistance to creep, compatible with the press, was designed and mounted.
- To measure the exact temperature in the sample and be perfectly in compliance with the standards EN ISO 1893 and EN 993 – 9, a thermocouple that can be inserted into the centre of the autoclave furnace and is thus located in the immediate vicinity of the sample under investigation was installed in the system.

3.1.2. *Developing the atmospheric control system*

The experimental testing device, which was used for the investigations, was already equipped with a basic system to control the atmosphere in order to perform measurements in various gas atmospheres (Argon, Nitrogen, air, mixture, etc.) or in vacuum. To achieve the reliability of operation that was deemed necessary for the investigation of creep behaviour at high temperature, the atmospheric control system was developed in several areas:

- In order to monitor the oxygen and carbon monoxide CO contents, the atmospheric control system was equipped with a gas analyser (IM 1440F, IM Env. Equip. Germany GmbH). During measurements in inert atmosphere, the increase of the CO content indicates that most likely a combustion reaction take place and therefore that, if no oxygen is directly measured by the gas analyser, oxygen “appears” in the autoclave.
- For specific measurements, especially so that oxygen sensitive products can be properly characterized, an oxygen-free atmosphere must be ensured. As a first potential source of undesired oxygen in the system, the tightness of the autoclave oven

had been called into question. With the help of a helium leak detection equipment, the presence of leakages was controlled and leaks eliminated.

- Further technical gases, which are used to flush the autoclave oven, are usually not perfectly pure and may represent another source of oxygen. To remove any traces of oxygen from the technical gases, a purification system (oxygen trap –Oxisorb®, Spectron Gas Control Systems GmbH) was installed in the gas supply line.
- The last identified potential source of oxygen is the fibre ceramics isolating lining from the experimental furnace. Like every oxide ceramic, ceramic fibres chemisorbed and physisorbed oxygen molecules, but usually this represents only negligible quantities. However due to the very high specific surface of a fibre ceramics isolation lining, significant quantities of chemisorbed and physisorbed oxygen may be released in the furnace atmosphere at high temperature. In order to prevent the progressive released of chemisorbed and physisorbed oxygen with increasing temperature at high temperature, an evacuation schedule was developed which includes drawing of vacuum at about 1000 °C during the initial heating process. At this temperature, the chemisorbed and physisorbed oxygen can be more easily extracted.

3.2. Developing a new method for optical investigation of the creep behaviour of refractory products

With the aid of an optical dilatometer of the experimental testing device, the two dimensional evolution of the sample during creep testing was observed in real time for the first time. The decisive feature relies on the implementation of the optical dilatometer in addition to the differential method (see chapter 3.1) to follow the deformation of the sample. The cylindrical sample is placed in the centre of a furnace provided with two windows on opposite sides (Fig. 7). On one side a halogen lamp illuminates the sample. On the other side, the shadow cast by the sample against the light source is recorded by a high-resolution CMOS camera (Fig. 7 (b)). At high temperature the heat radiation image of the sample is recorded (Fig. 7 (c)). Using the image of the CMOS camera, it is possible to precisely monitor the deformations of the sample while simultaneously applying a load up to high temperature. Compared to the differential method, the optical dilatometer allows not only recording the vertical (height) deformation of the sample, but also the horizontal deformation.



Fig. 7: Sample in the centre of the experimental furnace (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).

To achieve the reliability of operation that was deemed necessary for the investigation of creep behaviour at high temperature, the optical dilatometer was developed in several areas:

- The “optical path” was enlarged so that the spatial deformation of 36 x 36 mm samples could be optically assessed. Due to the coarse grain microstructure of refractory products, samples have to be significantly larger than the larger grains (typically 1-3 mm) they are made up.
- The optical dilatometer technology available on the experimental testing device was optimised to allow a precise measurement of the deformation from room temperature to 1700 °C (optimization of the image contrast, lamp switch-off temperature, ...).
- At high temperature, volatile compounds were released from the samples into the furnace atmosphere and tended to re-condense on the cold areas of the furnace. The “optical path” was consequently contaminated with condensed material. Condensation products on the viewing windows hamper the optical path and consequently hinder optical measurements. In to avoid or, at least, delay the condensation process, a flushing system for the “optical path” was continuously optimised.

With increasing temperature, gas density gradients and turbulences in the furnace atmosphere tend to affect the stability of the image recorded by the high-resolution CMOS camera. In addition, the “optical path” was flushed with gas to avoid that volatile compounds condensate and consequently hamper the measurements. This flush process may even magnify the turbulences. Consequently, the stability of the optical dilatometer was investigated first (see chapter 4.1), before it was used for examination of the creep behaviour of refractories.

3.3. Investigation of the creep behaviour of refractory materials

FGF focused on refractory materials for steel making applications, especially carbon containing materials, as well as other materials sensitive to oxidation such as SiC. For this kind of materials, the sensitivity to oxidation limits the use of most standard equipment for their

characterisation up to high temperatures. Accordingly, the upgraded experimental testing device was used for the investigations.

3.3.1. Description of the investigated materials

Magnesia refractory products (reference material)

Precursor of the Magnesia-carbon refractory products, magnesia refractory products have been extensively used formerly in steelmaking because of their high resistance against corrosion from basic slags (originally introduced in Bessemer process, then in Linz-Donawitz process for steel production). Magnesia refractory products, usually bricks, are made out of sintered magnesia and, to a lesser extent, out of fused magnesia [7]. Due to the high elasticity modulus and high thermal expansion coefficient of periclase, which is the main crystal phase that Magnesia bricks are made of, these refractory products are very sensitive to thermal stresses for instance caused by thermal shocks.

The development of the Magnesia-Carbon refractory products, which offset many shortcomings of the Magnesia bricks while preserving most of their intrinsic advantages, lead to a strong decline of the use of the Magnesia bricks for the manufacture of steel.

Due to their relative high purity, the Magnesia refractory products have been used in this project as reference material for the development of the experimental equipment and verification of the new experimental methods.

Magnesia-Carbon (MgO-C) refractory products

Due to their intrinsic properties and performance, Magnesia-Carbon refractories (MgO-C) have become established as a key component of steel production. Especially the carbon bond/fraction accounts for their outstanding resistance to corrosion and thermal stress. Since the successful introduction of the first carbon containing refractory products in the steel making industry, several different bonding systems and carbon carriers have been investigated. Nowadays, graphite and soot are the most common solid carbon carriers for commercial products. Different qualities of graphite are available with carbon content ranging from ~92 mass-% to 98,5 mass-% for special applications. The bond of shaped products is traditionally ensured by tar pitch. More recently, the use of synthetic resin as binder has made significant progress. Occasionally and for specific application, petroleum pitch may substitute tar pitch [4]. Further alternative such as coal-tar resin also show convincing results for industrial applications [5] [6]. Of course, each bonding system presents its own advantages and disadvantages, especially as regards to the toxicity and environmental issues or manufacturing processes (processing temperature, hardening and shaping) and service properties (resistance to corrosion and thermal stress).

Carbon-containing refractory products are composite materials where the carbon bond/fraction ensures an enhancement of their resistance against thermochemical and thermomechanical wear compared to their pure oxide counterpart. Because of the broad spectrum of raw materials, even without considering the oxide fraction, the service properties and lifetime of carbon containing refractory may greatly vary. The proper characterisation of the

material properties is therefore a crucial area of focus either for quality assessment and control issues or for the development of innovative carbon containing refractory products. However, the sensitivity to oxidation of the carbon fraction limits the use of most standard equipment for this characterisation. Especially over 800 °C, the carbon present in the carbon-containing refractory products reacts progressively with oxygen from the atmosphere to form gaseous carbon oxides, leaving only behind the oxide fraction with minimal cohesion and strength. The measured properties of the carbon containing refractory product are thus no longer representative of its service performance. Therefore, specific experimental testing devices for the characterisation of carbon containing refractory products under non-oxygen atmospheres were developed.

SiC containing unshaped refractory products (castables)

In addition to the intrinsic well known advantages of castables in handling, working and placement, SiC containing refractory castables display improved thermal shock resistance and resistance to abrasion. They are therefore widely used in thermal process equipment where these properties are required [8], for instance in heating systems using pellets, wood or chippings and in combustion plants and waste incinerators.

However, the SiC grains gradually oxidize at temperatures above 1000 °C in air, thereby the specific properties of the SiC containing refractory castables are progressively altered or even lost. The impact of the atmosphere is therefore a crucial parameter to be considered for proper characterisation of the material properties.

3.3.2. Preparation of samples

For the creep measurements, cylindrical samples (50 x 50 mm or 36 x 36 mm) were required. These samples were obtained from bricks or cast bars by drilling and machining with diamond tools. The axis of the cylinders drilled out of bricks or cast bars was laid parallel to press direction for bricks, which usually correspond to the direction of the main compressive loading in-service, or perpendicular to the cast direction for the SiC containing refractory castable. In order to use the differential testing method, a central hole was drilled in the middle of the cylinders parallel to cylinder axis.

To ensure that the upper and under surfaces of the sample were perfectly parallel, the as-drilled samples were fixed in a support developed for this purpose and machined to the required dimensions and tolerances using a high precision cut-off machine Brillant 290 from ATM (Germany). No further grinding step was found to be necessary.

4. Experimental results

4.1. Precision and accuracy of the new methods to determine creep behaviour of refractories

4.1.1. Precision

As a new method for investigation of the creep behaviour of refractory products, an optical dilatometer was implemented. The precision of the new method was experimentally assessed from repeated measurements under unchanged conditions. The standard deviation of these measurements was considered as the precision of the method.

The precision of the optical dilatometer might be influenced by flush gas flow that is necessary to keep the “optical path” clear according to chapter 3.2. Consequently, the precision of the optical dilatometer, using samples of 36 x 36 mm from the magnesia reference material, was determined at different temperatures and with different flush gas flow rates.

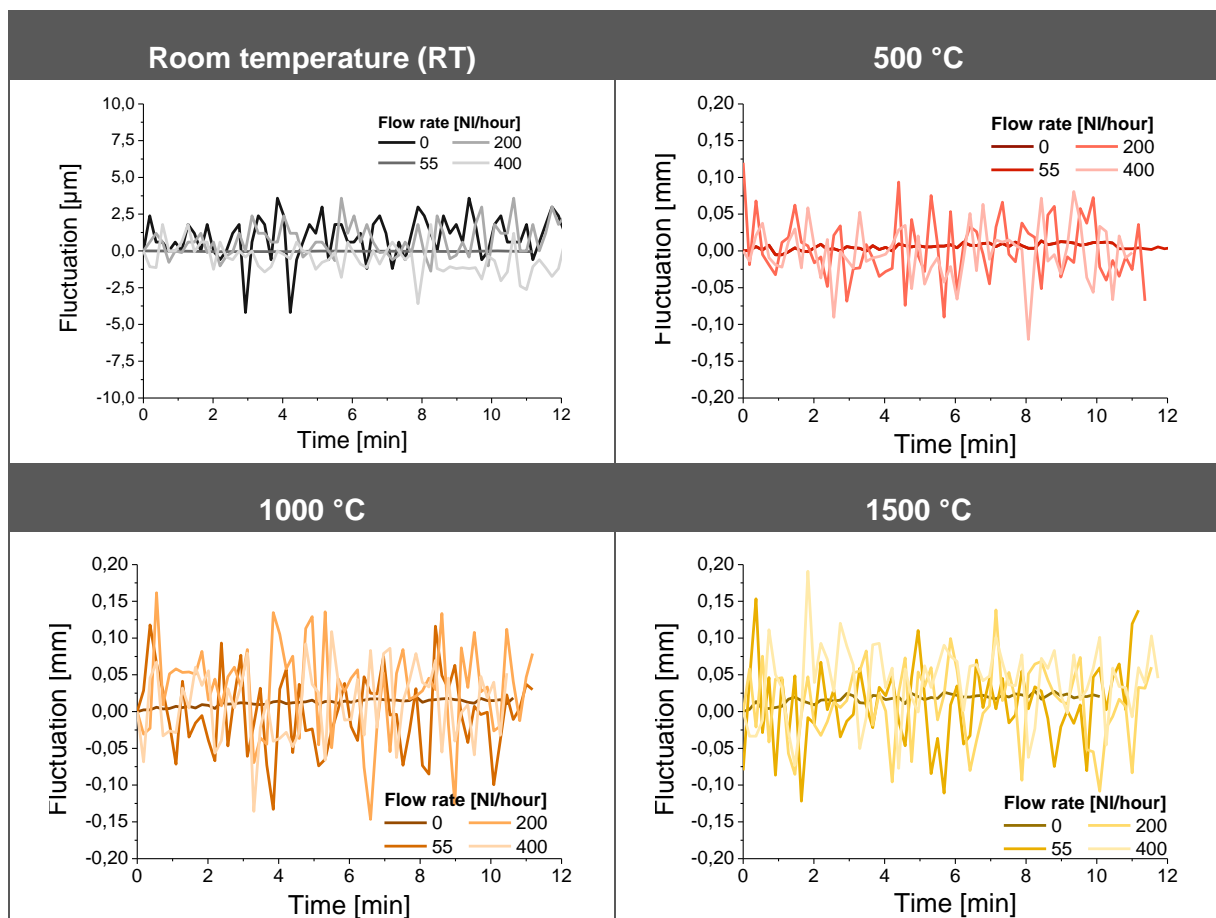


Fig. 8: Fluctuation in the measurement of the width of the reference sample as a function of the flush gas flow rate for different temperatures between room temperature and 1500 °C. Note the different scale of the y-axis of the graph showing behaviour at room temperature.

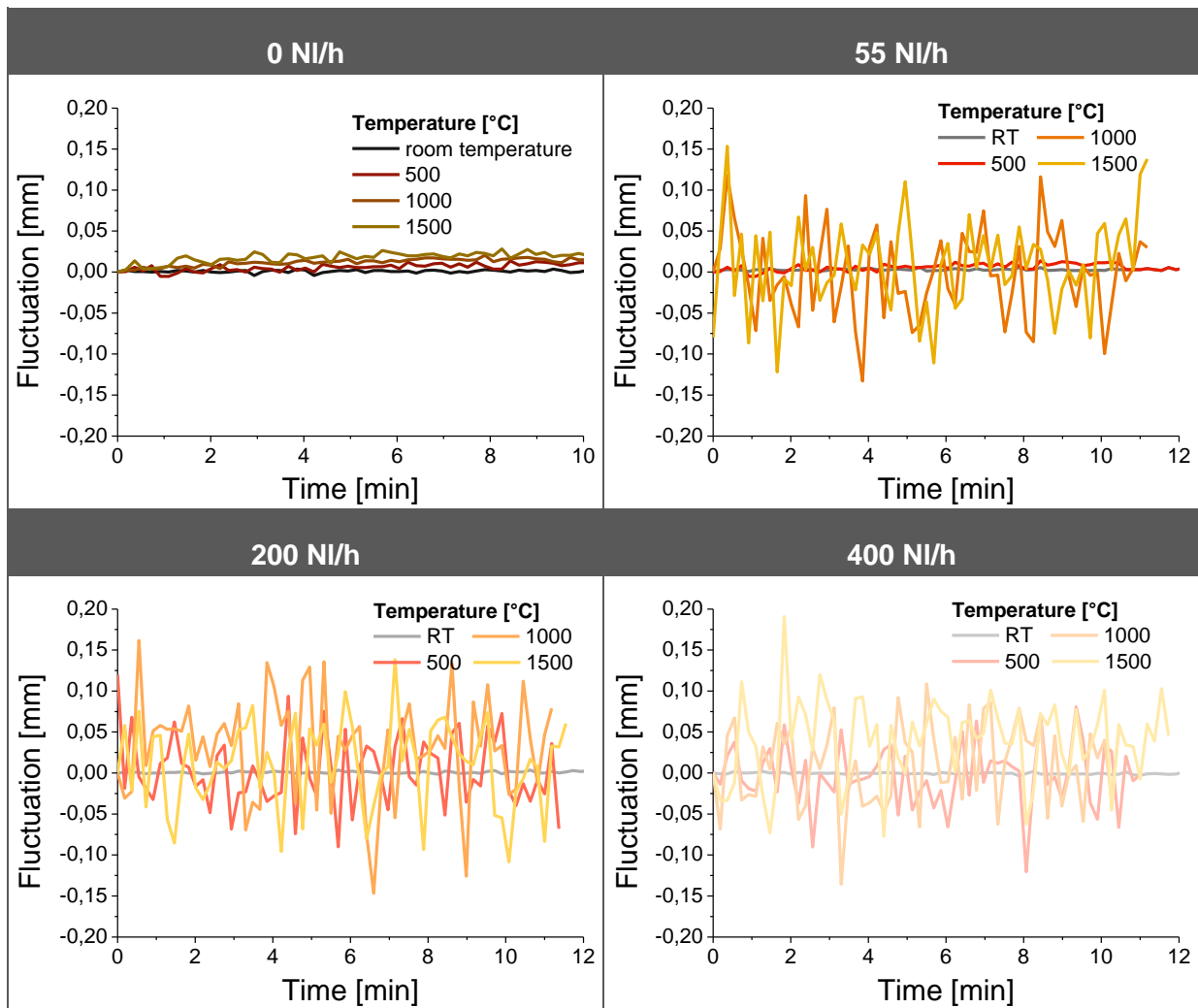


Fig. 9: Fluctuation in the measurement of the width of the reference sample as a function of the temperature for different flush gas flow rates.

Tab. 1: Standard deviation in μm (precision) of the new method for investigation of the creep behaviour of refractory products by optical observation, calculated from the measurements of the width of a 36 x 36 mm reference sample over 12 minutes.

Flush gas flow rate	Room temperature	standard deviation [μm]			
		500 °C	1000 °C	1300 °C	1500 °C
0 NI/h	0,73	2,69	2,73	8,6	7,22
55 NI/h	0,68	26,4	31,4	34,5	39,2
200 NI/h	0,65	25,9	37,5	35,5	30,9
400 NI/h	0,70	22,3	30,7	36,1	30,1

As expected, the stability of the optical method was found to be very good at room temperature with a standard deviation of approximately 0,7 μm . With flush gas flow, the standard deviation of the optical method increased with increasing temperature and reached 40 μm at 1500°C. Without flush gas flow (flow rate of 0 Nl/h , Fig. 9), the experimental precision was found to be only moderately impacted by the temperature and the standard deviation of the optical method increased only slightly to 7,2 μm at 1500 °C. In summary, above 500 °C, even low flush gas flow rates were found to lead to significant fluctuations and resulting large standard deviations of the measurements, whose magnitudes were apparently independent of the intensity of the flush gas flow rate.

The experimental precision of the differential method was assessed to circa 1,3 μm at 1500 °C, noticeably better than the optical method when flush gas is used and roughly comparable to the optical method without the use of flush gas at 1500 °C. However, since for the characterisation of the creep behaviour of refractory products, relevant deformations (thermal dilation up to circa 1 mm and subsidence greater than few millimetres) are more than two magnitudes greater than the standard deviation experimentally assessed (in worst case 40 μm) due to the large samples utilised in creep measurements, the precision of the optical dilatometer was deemed fairly acceptable. A higher precision of the optical method at high temperature could be realised by stopping the flush gas flow for periods of measurement.

4.1.2. Accuracy

As new methods for investigation of the creep behaviour of refractory products by differential method (see chapter 3.1) and by the new optical method (see chapter 3.2) were developed, the accuracy of these new methods was evaluated.

The accuracy of the methods was defined as the degree of closeness of measurements of a quantity to that quantity's actual (true) value (from standard testing methods).

The two new methods were thus compared to each other (optical method see Fig. 10) and to ISO (3187) and EN (993-9) standards, using samples of 36 x 36 mm from the magnesia reference material, a heating rate of 5 $\text{K}\cdot\text{min}^{-1}$ and an initial stress of 0,2 MPa.

Due to the relatively high purity of the reference sample no subsidence is observed on the refractoriness under load curves and only the thermal expansion of the sample was measured (Fig. 11). The coefficient of thermal expansion was estimated from the refractoriness under load curves to $1,39\cdot 10^{-5} \text{ K}^{-1}$ (differential and optical method) and was found to be consistent with values from the literature ($1,35\text{-}1,4\cdot 10^{-5} \text{ K}^{-1}$ [7]). In addition, both curves from the two new measurement systems (differential and optical) were found to fit very well with curves obtained with a standard system routinely used for RuL measurements (RUL/CIC 421 testing system from NETZSCH). The accuracy of both new methods was thus defined as very good.

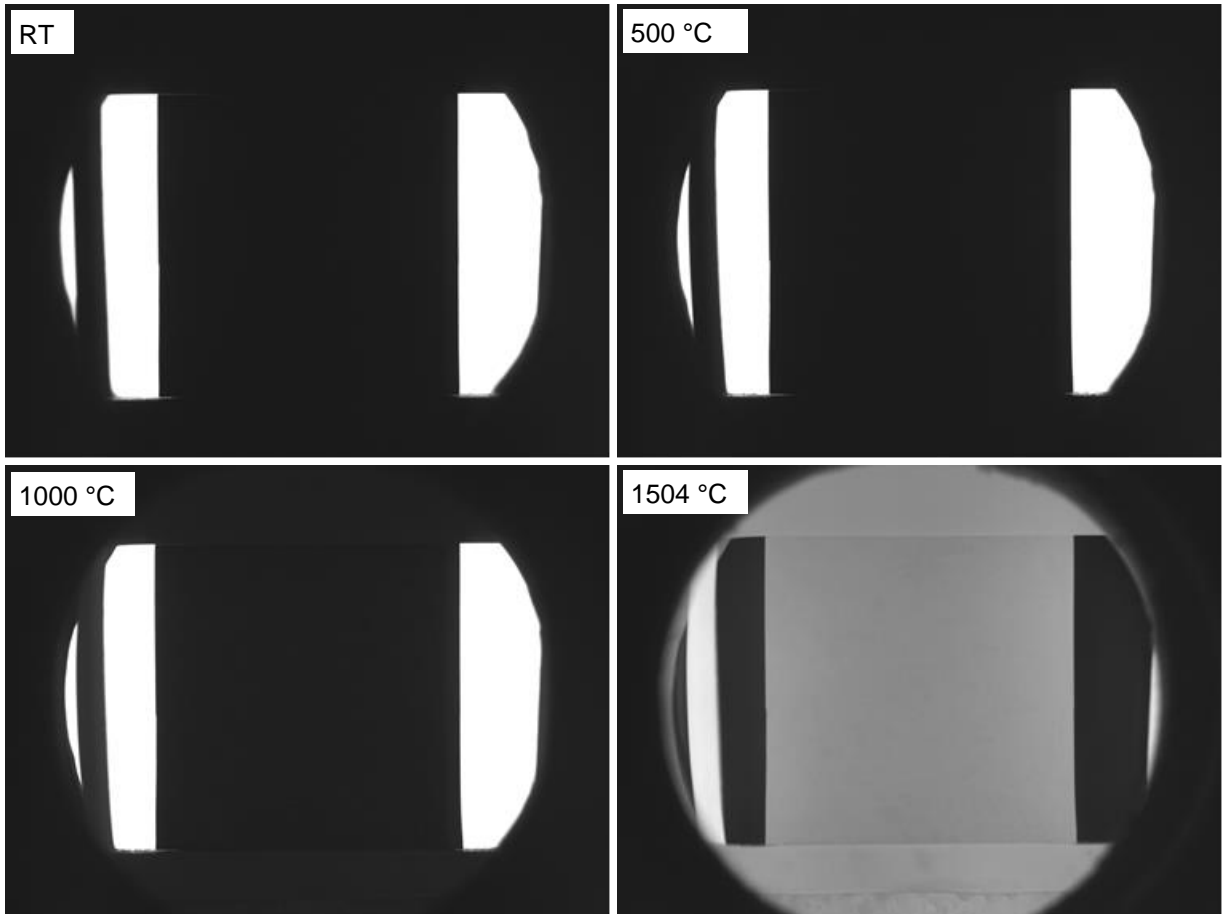


Fig. 10: Images of the CMOS camera (optical dilatometer) of a reference sample in course of a refractoriness under load (initial stress: 0,2 MPa, heating rate: 5 K.min⁻¹) measurement in oxidising atmosphere.

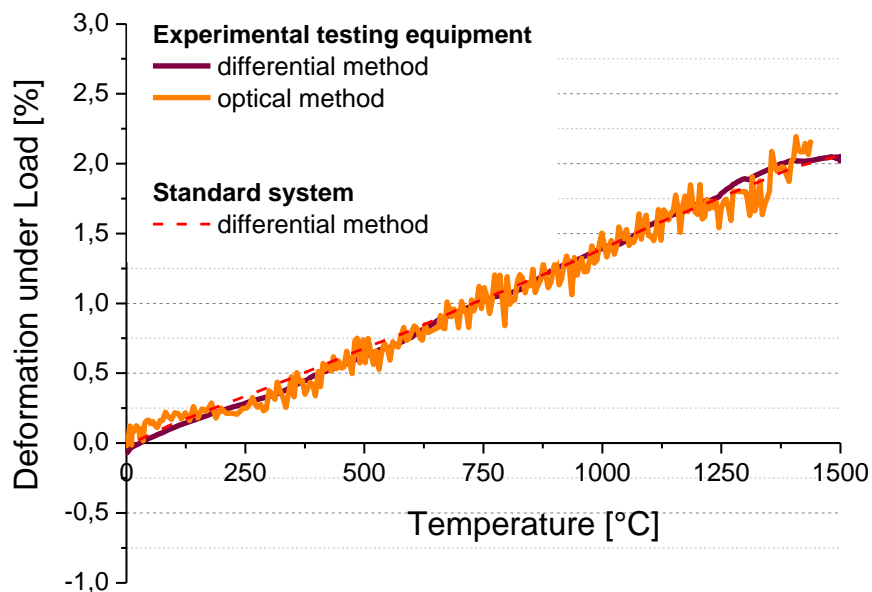


Fig. 11: Comparison of the refractoriness under load (initial stress: 0,2 MPa, heating rate: 5 K.min⁻¹) curves (reference sample) measured with the experimental testing device and a standard system in oxidising atmosphere.

4.2. Measurement of creep behaviour

4.2.1. Reference material (magnesia refractory product)

As a proven and well-known material, a magnesia refractory product was used in this project as reference material to support the development of the experimental equipment and the optical method. Besides its relative high purity (Tab. 2 – MgO content > 95 %), the selected magnesia refractory product had the advantage of consisting of relatively similar raw materials compared to the Magnesia-Carbon refractories used in the research (same producer). The main oxide phase for both refractories is periclase, cubic form of magnesium oxide (MgO).

Tab. 2: Chemical analysis of the reference magnesia refractory product.

Component	weight percent (wt.-%)	Component	weight percent (wt.-%)
Al ₂ O ₃	0,34	Na ₂ O	0,01
SiO ₂	1,61	K ₂ O	0,03
Fe ₂ O ₃	0,66	Cr ₂ O ₃	<0,01
TiO ₂	0,02	P ₂ O ₅	0,09
CaO	1,31	ZrO ₂	0,01
MgO	95,87		
Density [g/cm ³]	3,07		
Porosity [%]	13,3		

4.2.1.1. Refractoriness under Load (EN ISO 1893)

The coefficient of thermal expansion was estimated from the refractoriness under load curves (see section 4.1.2) to $1,39 \cdot 10^{-5} \text{ K}^{-1}$ (differential and optical method) and was found to be consistent with values from the literature ($1,35-1,4 \cdot 10^{-5} \text{ K}^{-1}$ [7]).

4.2.1.2. Determination of creep in compression (EN 993 - 9):

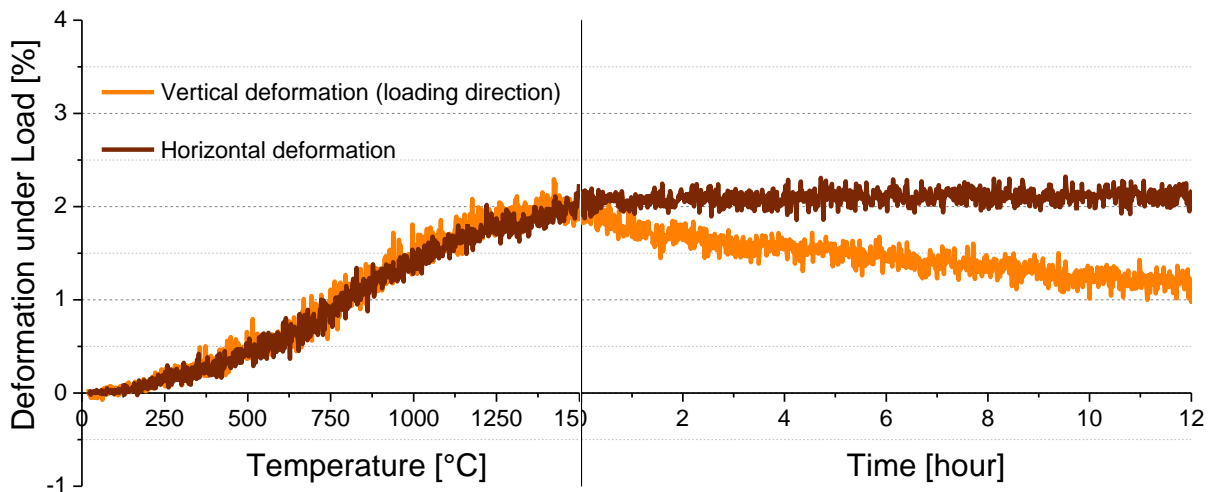


Fig. 12: Creep in compression (CiC) measurements at 1500 °C (initial stress: 0,2 MPa, heating rate: 5 K.min⁻¹, optical dilatometer - reference sample MgO) in oxidising atmosphere.

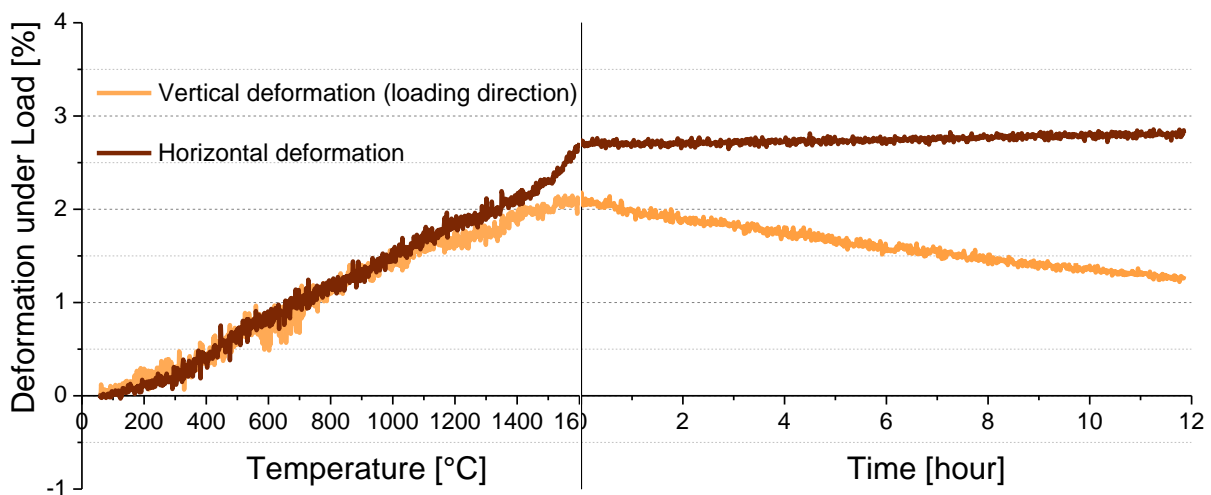


Fig. 13: Creep in compression (CiC) measurements at 1600 °C (initial stress: 0,2 MPa, heating rate: 5 K.min⁻¹, optical dilatometer - reference sample MgO) in oxidising atmosphere.

The first part of the CiC curves, i.e. during the rise in temperature of the sample (heating rate: 5 K.min⁻¹, initial stress: 0,2 MPa), was found to be basically identical to that observed for RuL measurement. In this part, the thermal expansion of the reference sample takes place. However, above 1450 °C, the first irreversible deformations were found to take place and the path of the two curves showing horizontal and vertical deformations started 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), are assumed to govern the creep behaviour of refractory products.

An increase of temperature lead to a slight increase of the creep rates after 12 hours (Figures 12 and 13 - Tab. 3). The amount of viscous phase is expected to increase with higher temperature, in addition the viscosity of the viscous phase also decreases with temperature, promoting the deformation of the reference sample.

Tab. 3: Creep rate v (% \cdot h $^{-1}$) after 12 hours for an initial stress of 0,2 MPa and different temperatures in oxidising atmosphere.

v (% \cdot 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

In the direction perpendicular to the loading direction (“horizontal deformation”), a slight swelling of the sample was measured. Although known before, this phenomenon could not be, until now, assessed and quantified during standard CiC measurements. 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 provided new decisive information, especially to support the development and verification of 3-dimensional models.

4.2.2. Magnesita-Carbon refractories (MgO-C)

As stated previously, the main challenge for the characterisation of carbon containing refractory products lied in the preservation of the carbon fraction of the refractory material.

In the course of the research project, a synthetic resin bonded magnesita-carbon brick was investigated. In presence of oxygen and at elevated temperature, the carbon present in the matrix burns off, leaving behind a MgO skeleton with only minimal ceramic bond that does not reflect the operating characteristics and properties of the MgO-C product:



Being able to work in inert atmosphere thanks to the optimisation of the atmospheric control system, the experimental testing device provided ideal condition to preserve the carbon fraction from burning off at high temperature. First tests showed that the burning of the carbon fraction could be widely avoided, the sample remaining completely black after RuL meas-

urements (Fig. 14). However, the formation of a white wool-like condensate was observed during the tests under Argon atmosphere and impeded the measurement with the optical dilatometer above 1400 °C (Fig. 15). According to XRD analysis, the wool-like condensate consisted quasi-exclusively of periclase (MgO) and is, in practice, known as secondary MgO.

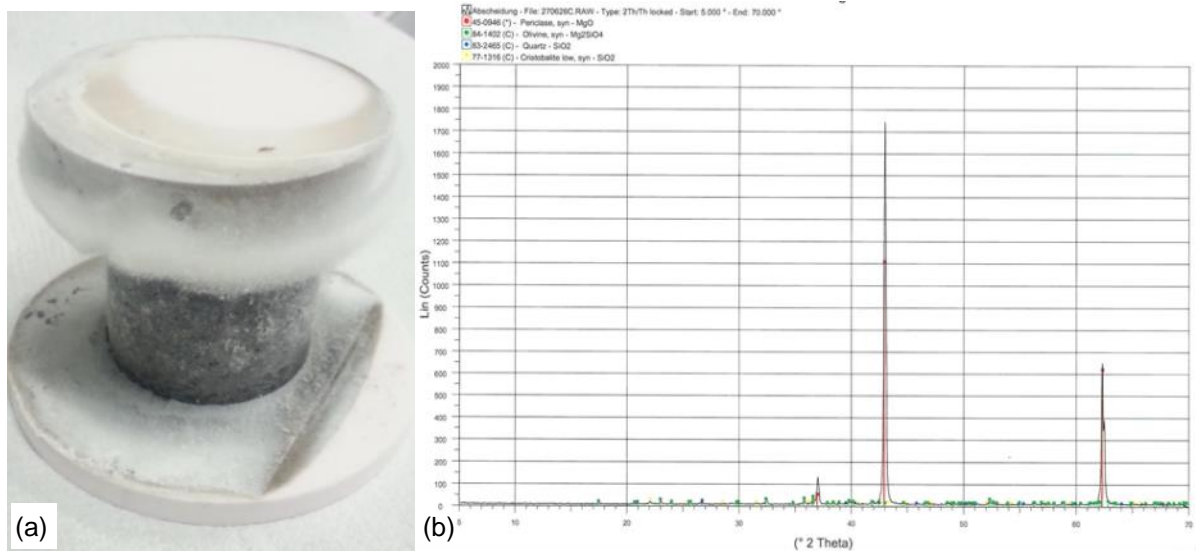


Fig. 14: (a) MgO-C sample after RuL in inert atmosphere (Argon) showing a wool-like condensate (b) XRD diagram of the wool-like condensate.

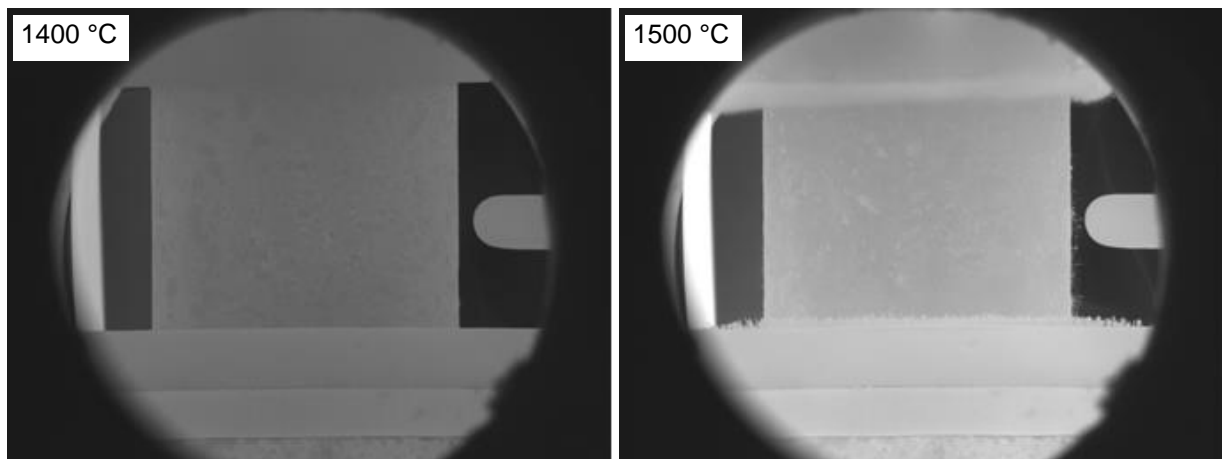


Fig. 15: Images of the CMOS camera (optical dilatometer) of the MgO-C sample in course of the RuL measurement in inert atmosphere (Argon).

Above 1400°C under low oxygen partial pressure, the carbon present in the MgO-C sample was found to react with the magnesium oxide according to the following reactions (carbo thermal reduction):

Direct reduction:



Indirect reduction:



This leads to the formation of gaseous magnesium which in turn reacts with oxygen to form magnesium oxide (secondary MgO), which was found as wool-like condensate:



This reoxidation reaction of the gaseous magnesium was found to take place even at very low partial pressures of oxygen, i.e. below 10^{-15} atm [10].

This carbo thermal reduction of magnesium oxide is typically observed for MgO-C bricks in service. The subsequent oxidation reaction of gaseous magnesium is even supposed to lead to the formation of a secondary MgO layer at the slag/brick or metal/brick interface that physically prevents penetration of MgO-C linings and enhances their service life. However, in order to use the optical dilatometer of the experimental testing device, the oxidation of gaseous magnesium and the subsequent generation of a wool-like condensate had to be prevented by further reducing the oxygen content in the experimental testing device (see chapter 3.1). As a result, only a minimal formation of secondary MgO on the surface of the sample was observed (figures 16 and 17).

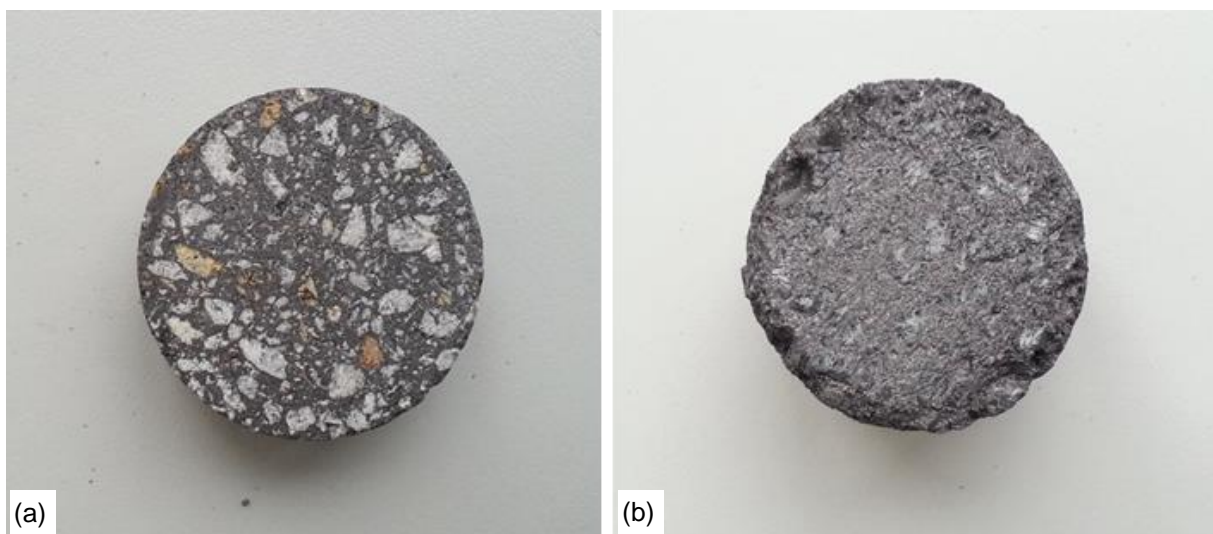


Fig. 16: MgO-C sample (b) before and (a) after RuL in inert atmosphere (Argon).

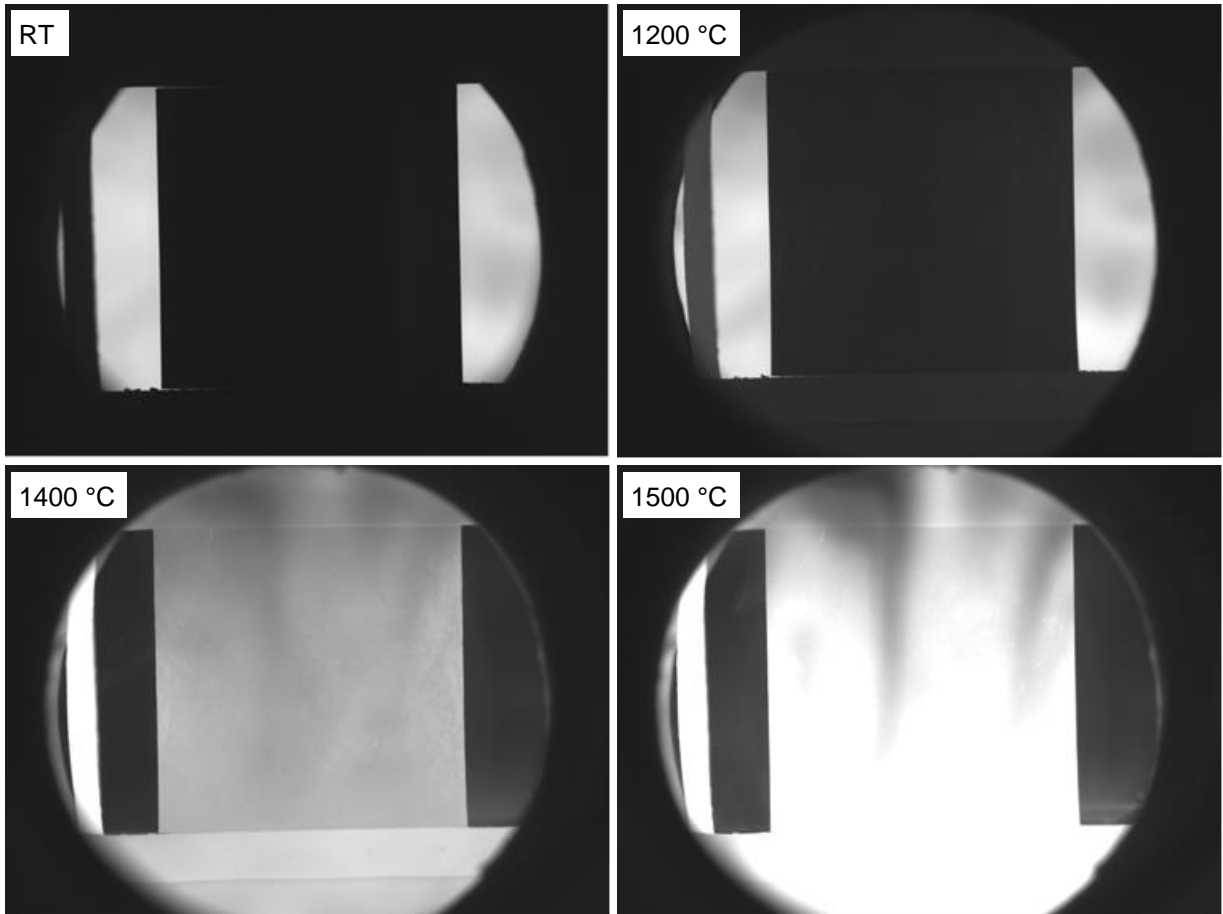


Fig. 17: Images of the CMOS camera (optical dilatometer) of the MgO-C sample in course of the RuL measurement in inert atmosphere (Argon).

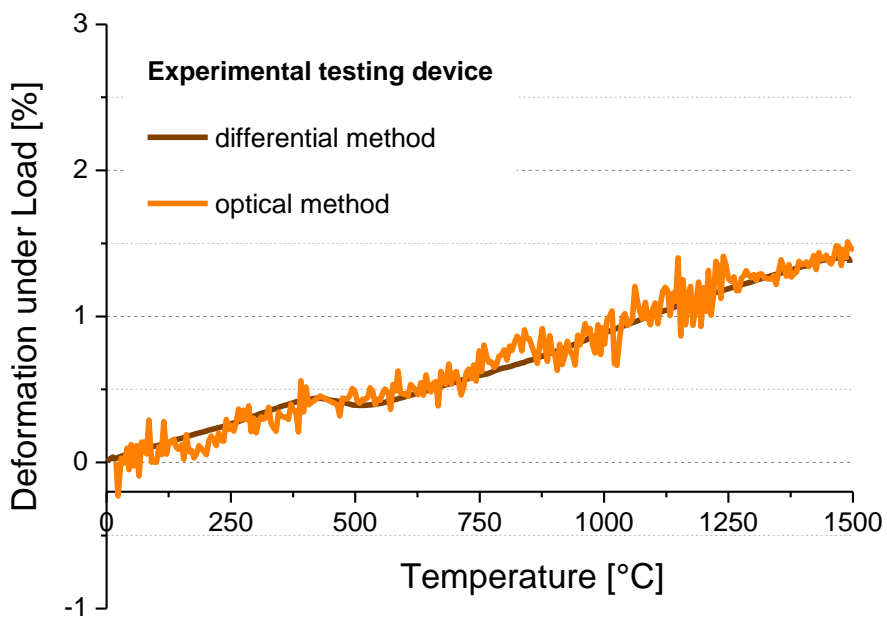


Fig. 18: Refractoriness under load (RuL) measurement of MgO-C sample in inert atmosphere (Argon)

Like for the reference material (Magnesia refractory product), no subsidence was observed on the RuL curves of the MgO-C sample (Fig. 18). Since both products are based on the same raw material (MgO - periclase crystals, Tables 2 & 4) and since carbon neither melts nor reacts with other oxides to form a viscous phase at high temperature, the similar behaviour with respect to the absence of subsidence was clear. Indeed, the microstructure of the MgO-C sample remained widely unaffected by the high temperatures during testing. Merely the finer grains of periclase were found to be reduced by the carbon fraction at the edge of the samples (Fig. 19). Offering a larger specific surface area, the fine grains of periclase were more easily reduced by the relative reactive amorphous carbon than the larger periclase grains. Graphite flakes and the large periclase grains were however largely spared and still were present at the edge of the samples after the RuL measurement. Besides, the core of the sample was widely left intact (Fig. 19). The carbo thermal reduction of the periclase grains may, in fact, also occur in the core of the sample. But the diffusion of the reaction products ($Mg_{(g)}$, $CO_{(g)}$ or $CO_{2(g)}$) becomes increasingly difficult with increasing distance from the edge of the sample (path of gas diffusion longer and more tortuous). As a result the partial pressure of $Mg_{(g)}$ increases and the carbo thermal reaction equilibrium is shifted to the left (Le Chatelier's principle). The reaction kinetic is slowed, if not completely impeded.

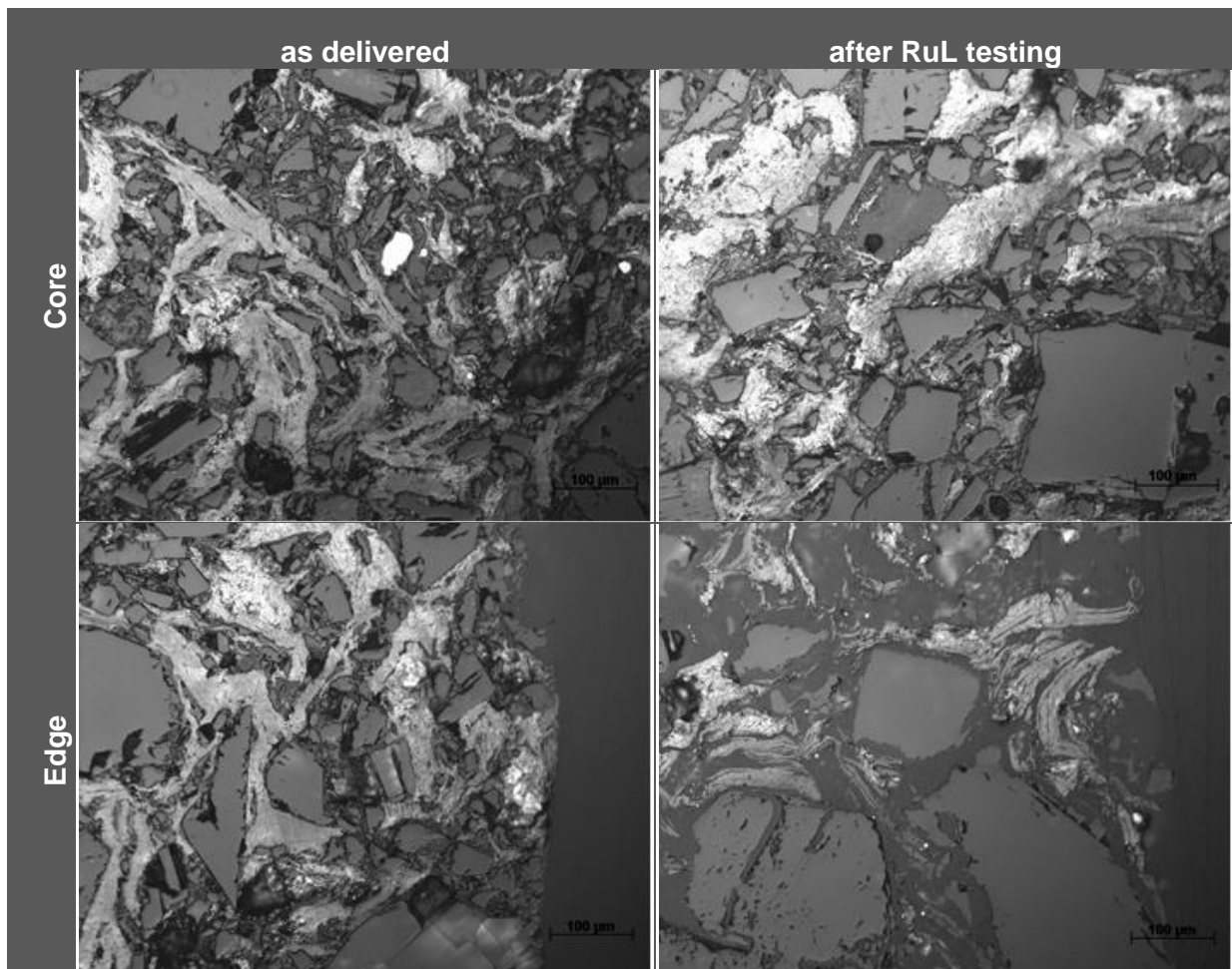


Fig. 19: Microstructural observations of the core and edge of the investigated Magnesia-Carbon refractory product (MgO-C) as delivered and after RuL testing.

In comparison to the reference (Magnesia refractory product) sample, the observed dilatation on MgO-C samples was clearly lower, due to the much smaller coefficient of thermal expansion of carbon (mostly graphite with an amorphous fraction) as compared to that of periclase. Finally the small contraction observed by 400-500 °C during RuL testing of MgO-C was linked to the pyrolysis of volatile constituents from the synthetic resin bond, since the brick was tested as delivered. The pyrolysis of volatile constituents accounted for a difference on the loss on ignition of circa 3 % between samples as delivered and after RuL testing (Tab. 4).

Tab. 4: Chemical analysis (oxidic components) of the investigated Magnesia-Carbon refractory product (MgO-C)

Component	weight percent (wt.-%)	
	as delivered	after RuL
Al_2O_3	0,51	0,45
SiO_2	1,08	1,07
Fe_2O_3	0,71	0,69
TiO_2	0,01	0,01
CaO	1,21	1,22
MgO	96,35	96,43
K_2O	0,01	0,01
Na_2O	0,03	0,03
Mn_3O_4	0,04	0,04
Cr_2O_3	<0,01	<0,01
P_2O_5	0,05	0,05
Loss on ignition [%] (1025 °C)	13,26	10,06

4.2.3. SiC containing unshaped refractory products

Having verified that the experimental testing device was operational and proficient for the reference MgO and MgO-C specimens, a more extensive study was carried out on 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 composition can experience varying operating conditions. For instance in thermal process equipment, the atmosphere may vary from oxidising to very low partial oxy-

gen pressure and even reducing in a single process cycle. Thereby the experimental testing device was found to be particularly suitable for a sound and extensive characterisation of SiC containing refractory castables.

According to chemical analysis (Tab. 5) and XRD and microstructural observations (Fig. 20), 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 characterisation of the creep behaviour, 36 mm x 36 mm cylinders were prepared by drilling and cutting unfired cast samples.

Tab. 5: Chemical analysis and density, porosity after curing at 1000 °C of the commercial SiC containing refractory vibrating castable

Component	Weight-%
Al₂O₃	48
SiO₂	25
CaO	2,5
SiC	20
Fe₂O₃	<1,0
<hr/>	
density [g/cm³]	2,55
Porosity [%]	<18

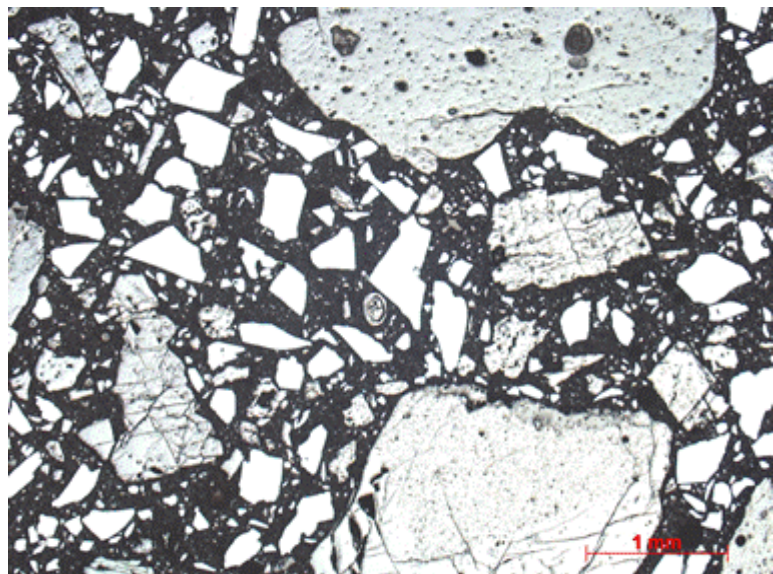


Fig. 20: Microstructural observation of the SiC containing refractory castable after drying.

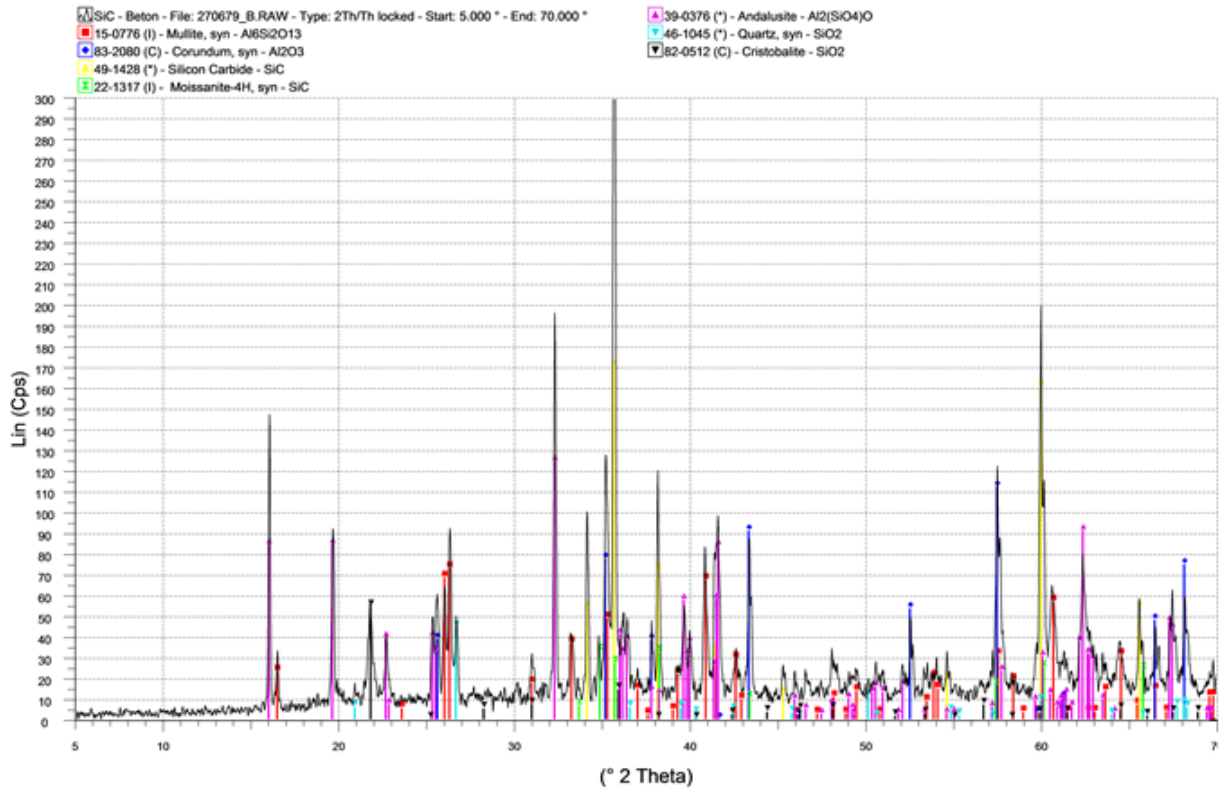


Fig. 21: XRD Diagram of the commercial SiC containing refractory vibrating castable after drying.

4.2.3.1. Refractoriness under Load

Using the specifications defined in the testing standards EN ISO 1893 and the differential method in the experimental testing device but varying the atmosphere, the impact of the atmosphere was examined (Fig. 22 and Table 6). Up to about 1300 °C, both curves were found to display a similar course, showing basically the thermal expansion of the samples. The first light subsidence by 250-350 °C was attributed to the drying shrinkage of the castable, where a major part of hydration water of the calcium aluminate hydrates is removed. Above 900 °C, the formation of new mineral phases from the remaining hydrate phases (e.g. calcium hexaaluminate CA₆) or from solid-phase reactions (e.g. mullite) was found to affect the volume stability of the system, resulting in slight subsidence on the RuL curves.

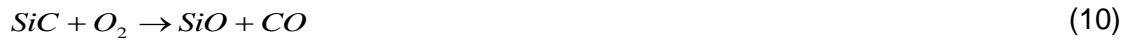
Until circa 1000 °C, the SiC contained in the sample did not suffer from exhaustive oxidation, even under oxidising atmosphere, thanks to the formation of a dense SiO₂ film on the surface of the SiC grains (“passive” oxidation):



Above 1250 °C, a viscous phase was slowly being formed and caused the softening of the sample. In oxidising atmosphere, the dense SiO₂ film grew with increasing temperature [11]

and may have reacted with impurities to form more viscous phase directly at grain boundaries, thus promoting the softening of the sample under oxidising atmosphere.

In contrast, under low partial oxygen pressure, the “active” oxidation of SiC took place above 1000 °C and lead to the formation of volatile SiO:



Although difficult to quantify, the presence of more viscous phase in samples tested in oxidising atmosphere was basically confirmed by a more pronounced coalescence of the pores after RuL measurements (Fig. 23). More viscous phase usually promotes the densification of ceramic systems.

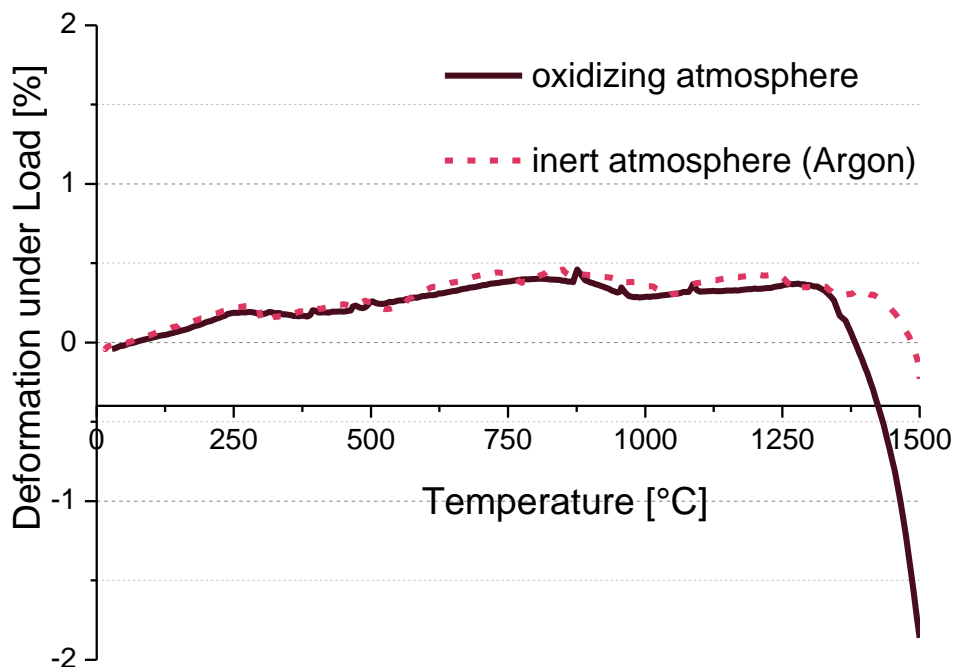


Fig. 22: Comparison of the refractoriness under load (RuL) curves of the commercial SiC containing refractory vibrating castable measured in oxidising and inert atmosphere.

Tab. 6: Temperatures corresponding to characteristic degrees of deformation.

	in oxidising atmosphere	in inert atmosphere
T_{0,5} (°C)	1407	1499
T₁ (°C)	1444	>1500
T₂ (°C)	1493	>1500

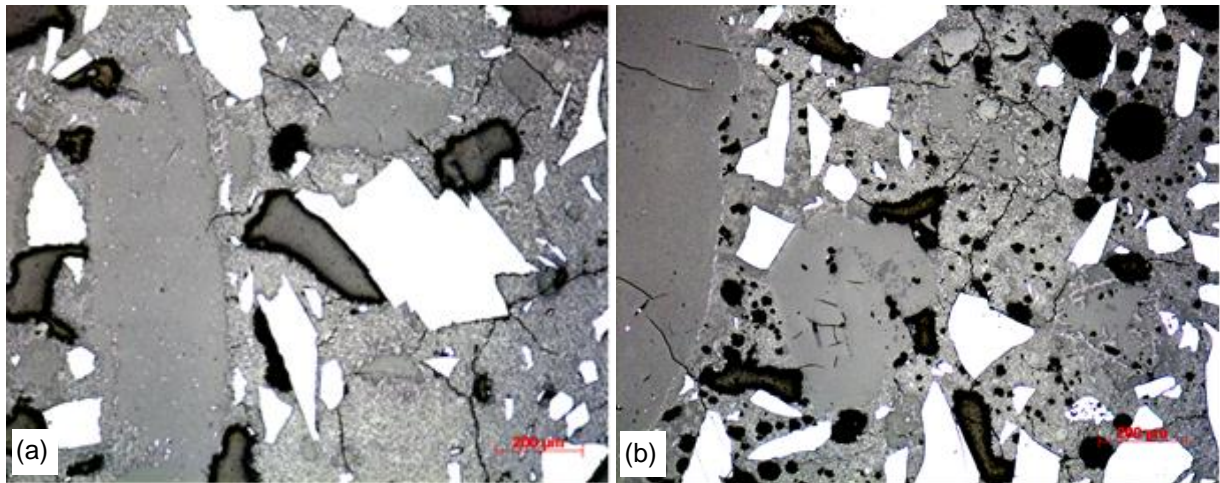


Fig. 23: Microstructural observation of the SiC containing castable after RuL testing (maximum temperature 1600 °C) in (a) oxidising atmosphere and (b) inert atmosphere.

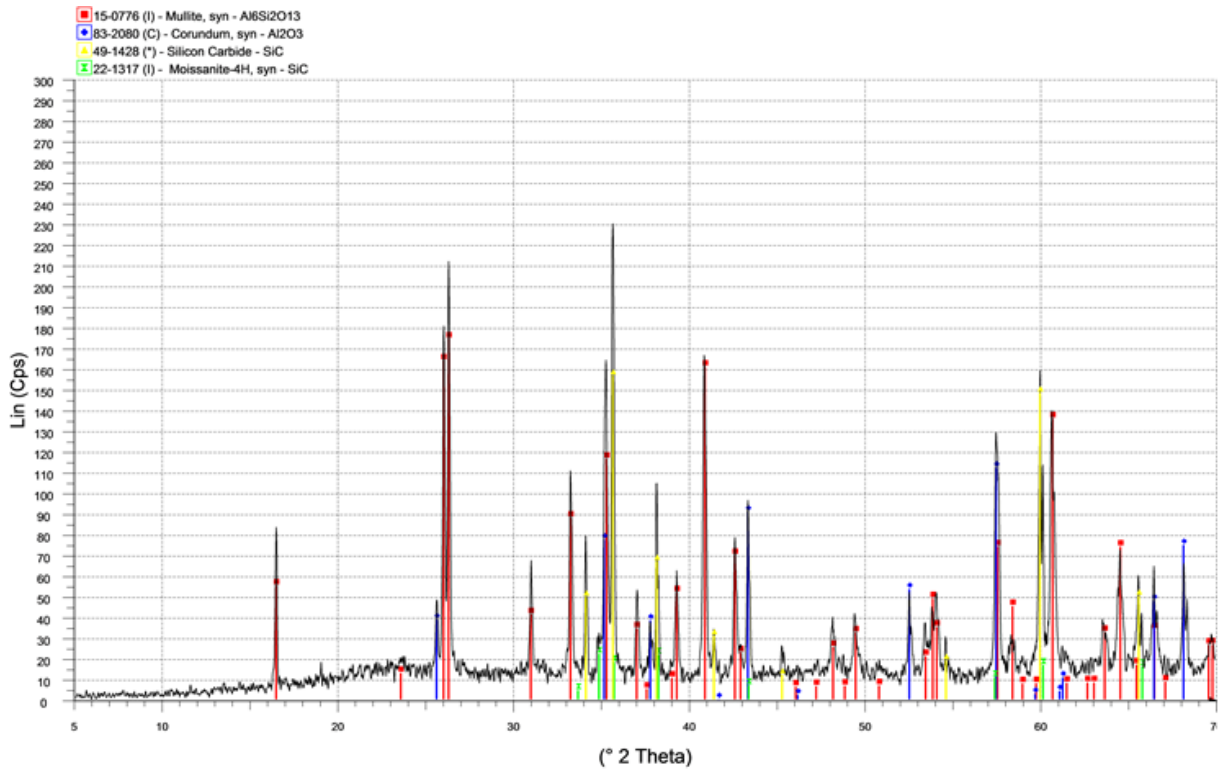


Fig. 24: XRD diagram of the SiC containing refractory castable after RuL testing (maximum temperature 1600 °C) in oxidising atmosphere.

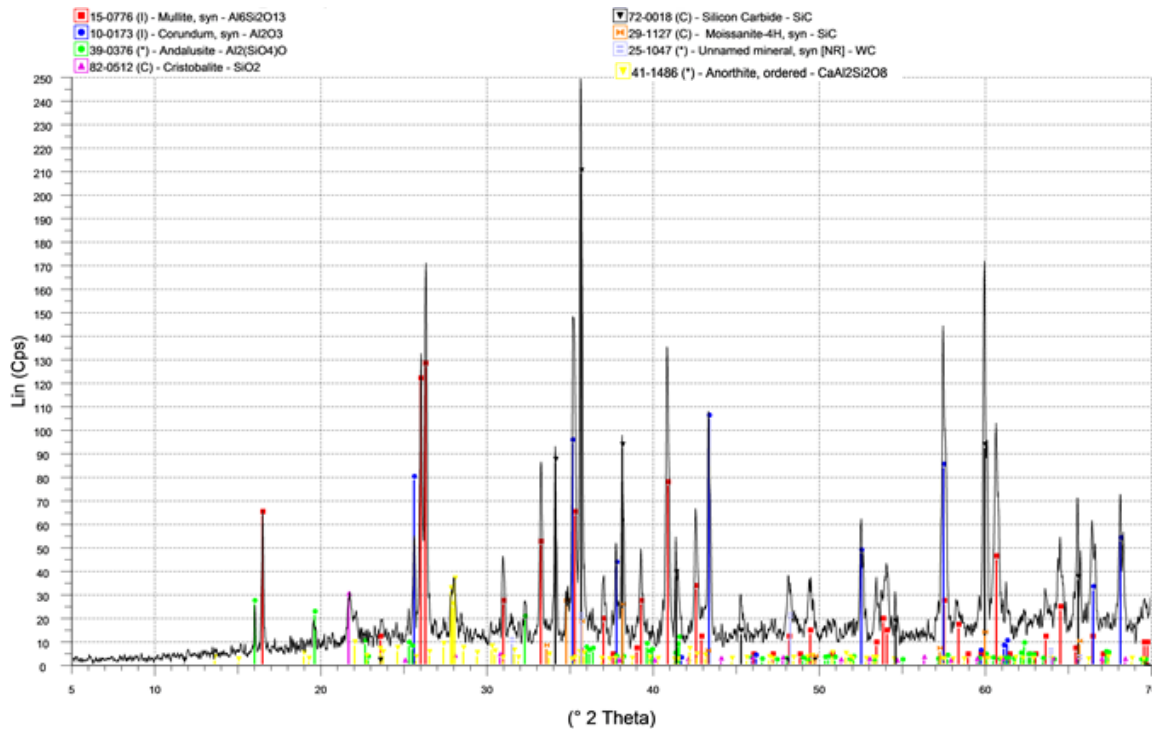


Fig. 25: XRD diagram of the SiC containing refractory castable after RuL testing (maximum temperature 1600 °C) in inert atmosphere.

Considering the crystalline phases, the pure silicate phases, quartz and cristobalite, as well as andalusite that were present in the sample before RuL measurements (Fig. 21), reacted at high temperature during the measurements to form mullite (figures 24 and 25) and in all likelihood a viscous phase.

After RuL testing in oxidising atmosphere, the XRD peaks showing quartz, cristobalite, and andalusite completely disappeared from the XRD diagram of the tested sample, whereas the intensity of the mullite peaks increased (Fig. 24). The intensity of the SiC peaks was also notably reduced, confirming the progressive oxidation of the SiC grains at high temperature.

After RuL testing in inert atmosphere, small XRD peaks indicating the presence of cristobalite and andalusite in the sample were still identifiable on the XRD diagram of the SiC containing refractory castable (Fig. 25). Consistently, the increase of the intensity of mullite peaks in inert atmosphere was found to be lower compared to the increase of the intensity after RuL testing in oxidising atmosphere. The atmosphere was therefore deemed to affect the reactivity of the system. In fact, in oxidising atmosphere, the passive oxidation of the SiC grains lead to the formation of amorphous SiO₂ at the grain boundary. At the testing temperature, amorphous SiO₂ reacted with the fine grain in the matrix to form new mullite. With its protective amorphous SiO₂ film weakened, the passive oxidation of the SiC grains was further promoted. In contrast, under inert atmosphere, mainly volatile SiO formed as a result of the active oxidation of the SiC. On the one hand, volatile SiO seemed to display a relatively low reactivity with the matrix or even to be conveyed out of the sample. On the other hand, in consequence of the active oxidation, and unlike passive oxidation, SiC grains progressively lost direct contact with the matrix (Fig. 29). Both processes explained the apparently lower reactivity of the system in inert atmosphere.

4.2.3.2. Creep in compression

Creep tests under constant load (0,2 MPa) were performed at different temperatures for both oxidising (air) and inert (Ar) atmospheres (Figures 26, 27 and 28). The creep rates measured during these tests in quasi steady state after 12 hours (quasi linear part of the curve) are given in table 7. 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 hours) 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 oxidising atmosphere compared to inert atmosphere. Microstructural observations showed that a more intensive densification was achieved in oxidising atmosphere (Fig. 29).

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

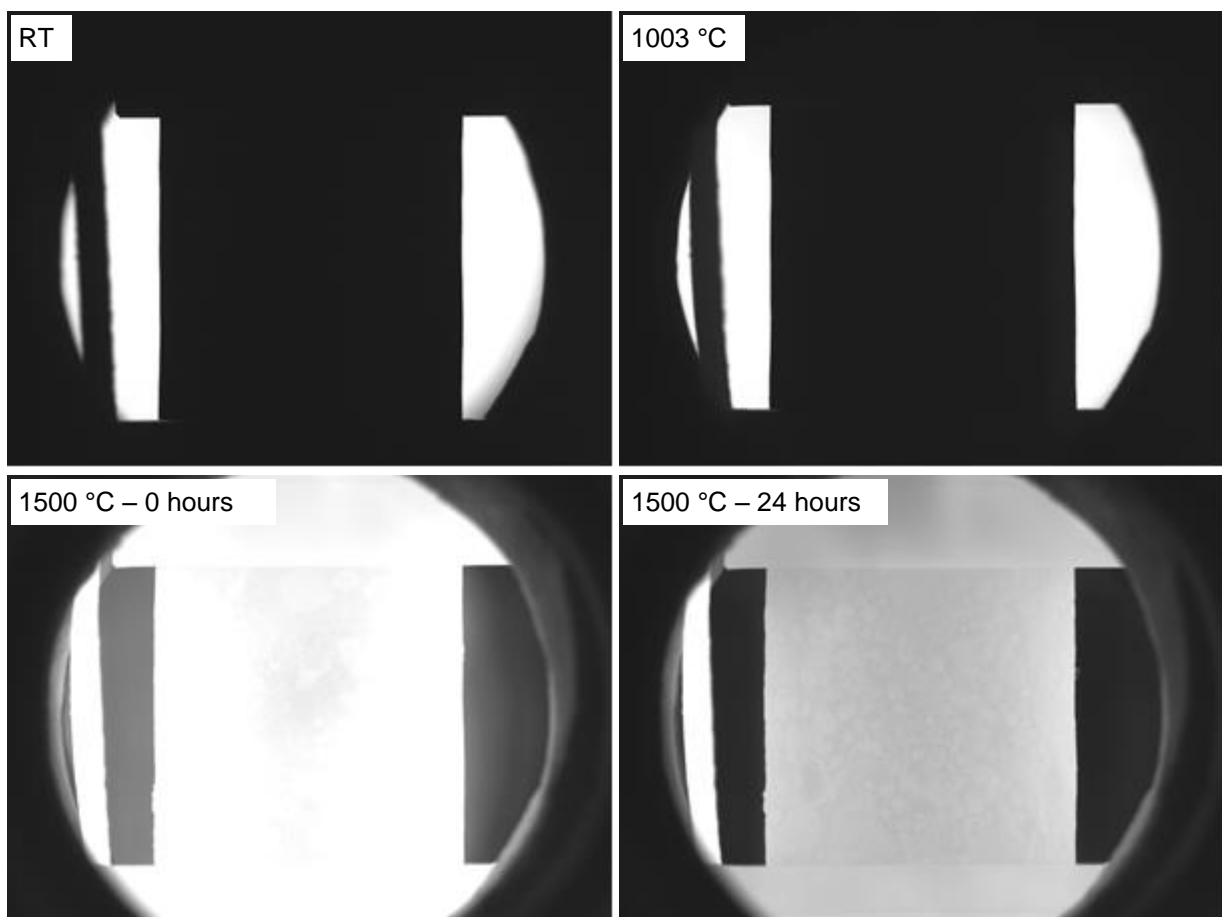


Fig. 26: Images of the CMOS camera (optical dilatometer) of the SiC containing castable in course of the CiC measurement (24 hours at 1500 °C).

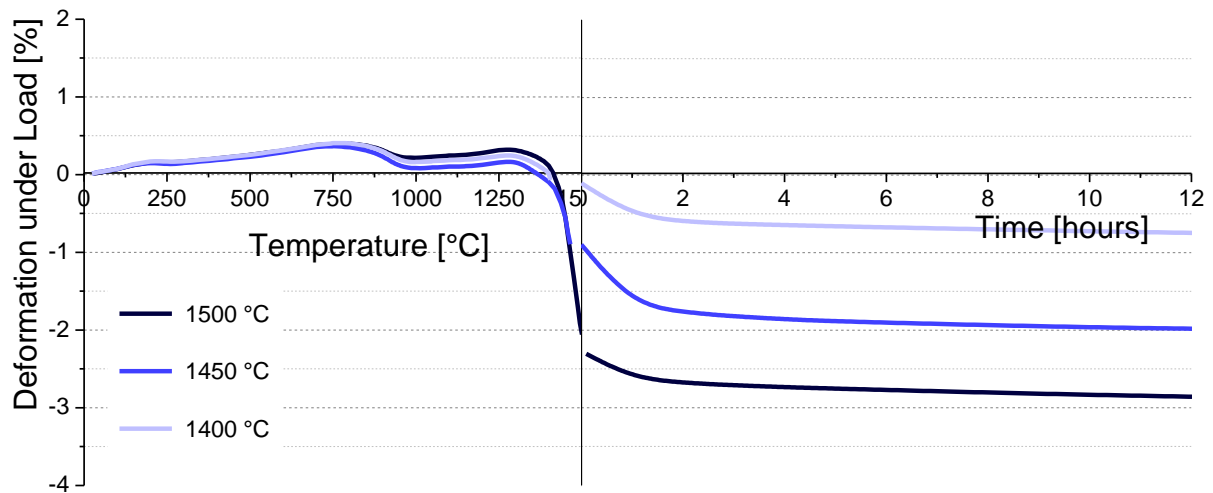


Fig. 27: Creep in compression measurements of the SiC containing castable at 1400 °C, 1450 °C and 1500 °C in oxidising atmosphere.

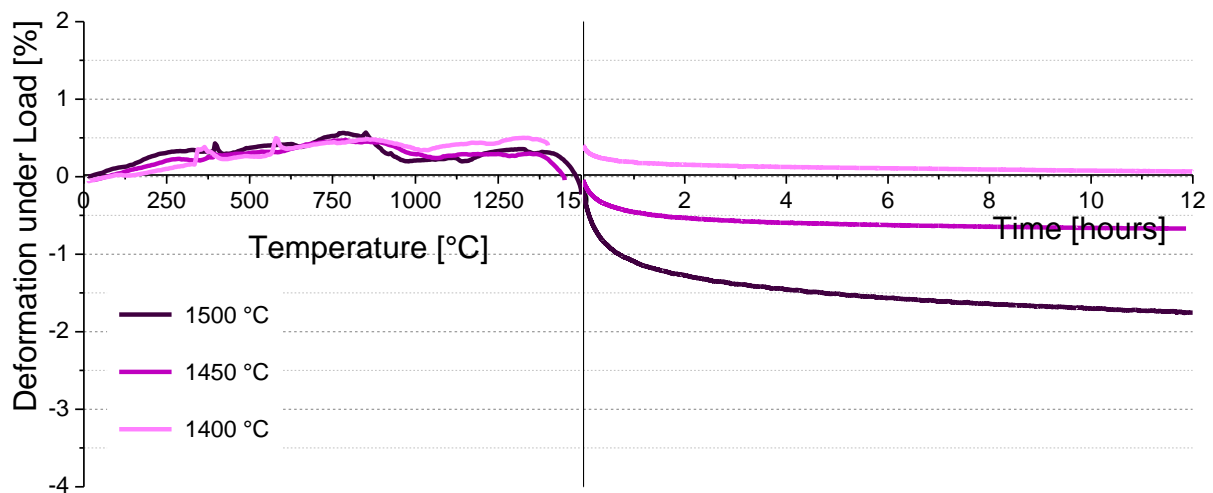


Fig. 28: Creep in compression measurements of the SiC containing castable at 1400 °C, 1450 °C and 1500 °C in inert atmosphere.

Tab. 7: Creep rate ($\% \cdot h^{-1}$) in quasi steady state (“secondary creep” after 12 hours) for an initial stress of 0,2 MPa, different temperatures and different atmospheres.

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

With regards to the crystalline phases, the evolution of the SiC containing castable system after the CiC measurements was found to be similar to the evolution observed for RuL measurements. Despite a lower maximum temperature, but with a longer exposure time, the

rest quartz, cristobalite, and andalusite phases present in the SiC containing castable before CiC testing reacted to form mullite and very likely a viscous phase. Indeed, the quartz, cristobalite, and andalusite XRD peaks were found to be gone on the XRD diagram of the tested sample after 24 hours CiC testing at 1500 °C in oxidising (Fig. 30) as well as in inert atmosphere (Fig. 31). In parallel the intensity of the mullite peaks grew while the intensity of the SiC peaks decreased.

Once again, the intensity of the mullite XRD peaks was found to be higher after testing in oxidising atmosphere compared to testing in inert atmosphere. For the intensity of the SiC and corundum XRD peaks, this was again the other way around. This confirmed the higher reactivity of the system in oxidising atmosphere, as previously discussed (see chapter 4.2.3.1).

Finally the presence of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$ or CAS_2) after testing in inert atmosphere (figures 24 & 30) or rather its absence after testing in oxidising atmosphere (figures 25 & 31) was linked to the increased reactivity of the system in oxidising atmosphere, at least its capacity to release SiO_2 . Anorthite may locally be formed whatever the atmosphere above 1300 °C in the calcium hydrate containing matrix of the SiC containing castable according to the ternary phase diagram of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. However, at the testing temperature, the release of additional SiO_2 as a result of the passive oxidation of the SiC grains in oxidising atmosphere was expected to shift the local equilibrium out of the stability field of anorthite.

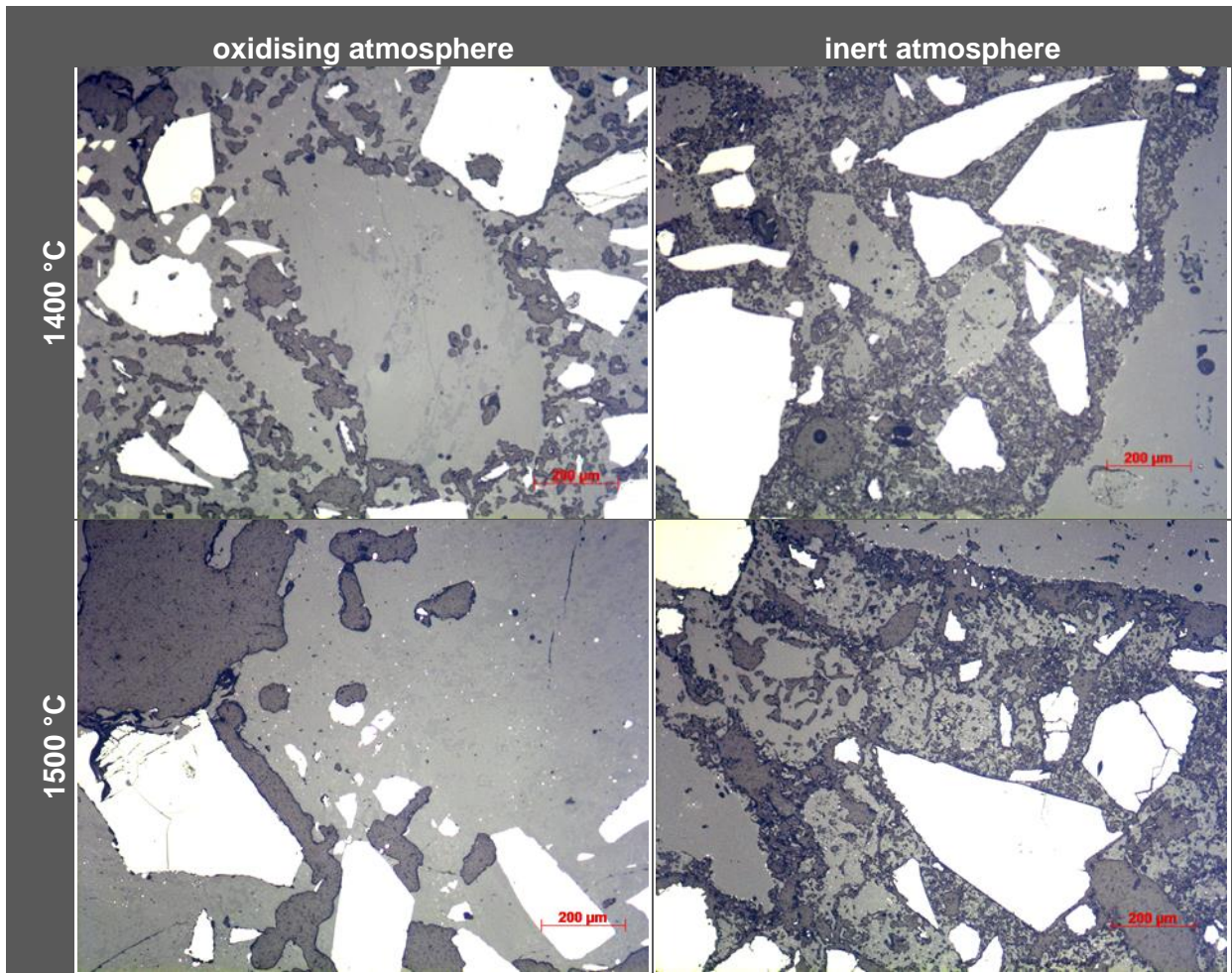


Fig. 29: Microstructural observation of the SiC containing castable after 12 hours CiC measurements at different temperatures for oxidising (air) and inert (Argon) atmosphere.

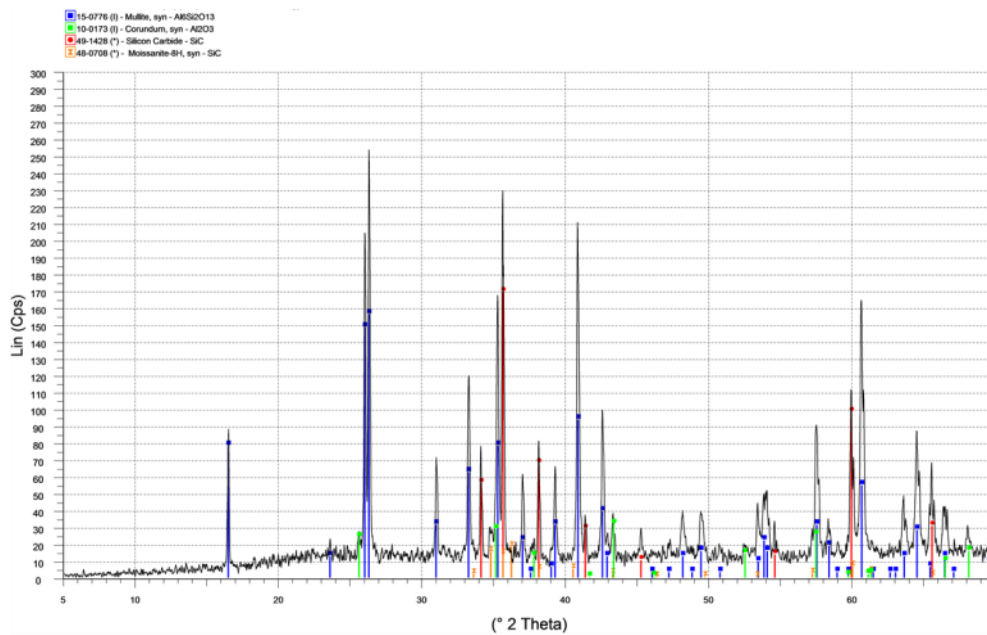


Fig. 30: XRD diagram of the SiC containing refractory castable after Creep in compression (CiC) measurements, 24 hours at 1500 °C in oxidising atmosphere.

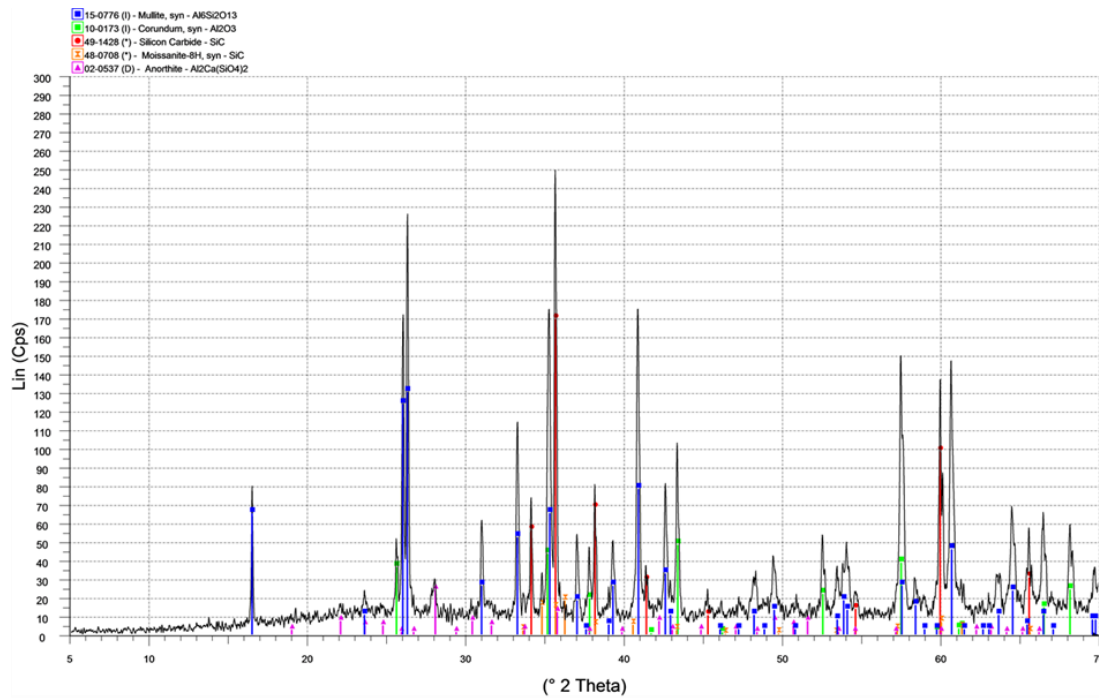


Fig. 31: XRD diagram of the SiC containing refractory castable after Creep in compression (CiC) measurements, 24 hours at 1500 °C in inert atmosphere.

The impact of the initial stress on the deformation levels 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 levels (Fig. 32). By contrast, the effect of the initial stress on the creep rates in quasi steady state (after 12 hours) was found to be much less obvious (Tab. 8).

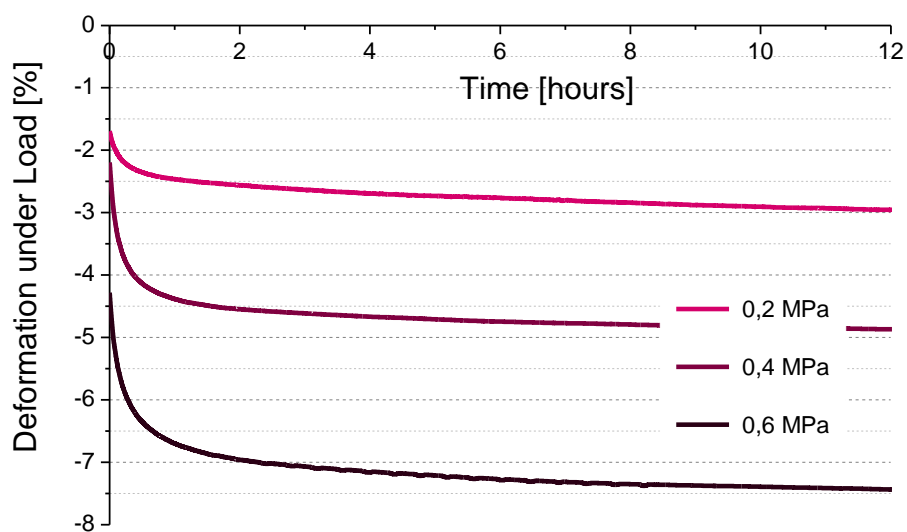


Fig. 32: Creep in compression measurement at 1500 °C in oxidising atmosphere for three different initial stresses of 0,2 MPa, 0,4 MPa and 0,6 MPa.

Tab. 8: Creep rate ($\% \cdot h^{-1}$) in quasi steady state (“secondary creep”) at 1500 °C in oxidising 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
Oxidising atmosphere	0,016	0,009	0,012

Through preventing 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 oxidising atmosphere (Figures 27 and 28). At 1500 °C, the creep rate after 12 hours in inert atmosphere clearly exceeded the creep rate in oxidising atmosphere (Tab. 7). 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. 29). In comparison, the relatively denser microstructure obtained under oxidising 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. 32) 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 (Fig. 33) practically impeded further deformations. The creep rates in quasi steady state (after 12 hours) did not show a clear dominant trend with increasing initial stress level (Tab. 8).

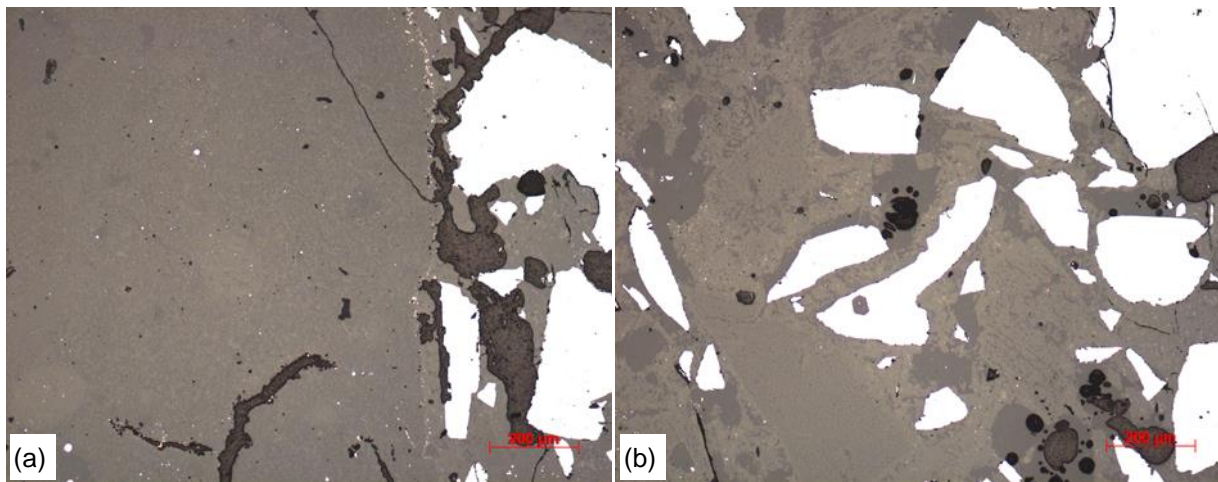


Fig. 33: Microstructural observation of the SiC containing castable after CiC measurement (24 hours at 1500 °C) in oxidising atmosphere, initial stress of (a) 0,2 MPa (b) 0,6 MPa.

Thermo-optical measurements, carried out with the optical dilatometer, were again found to be in good agreement with the measurements from the differential method (Fig. 34). In addition, for the first time, the horizontal deformations during CiC tests were quantified. The horizontal deformation near to the top and the bottom of the cylindrical sample turned out to be

significantly smaller than the deformations in the middle of the sample where the sample is free to expand (Fig. 34). These observations were in agreement with the visual examination of the samples, which took the typically barrel shape.

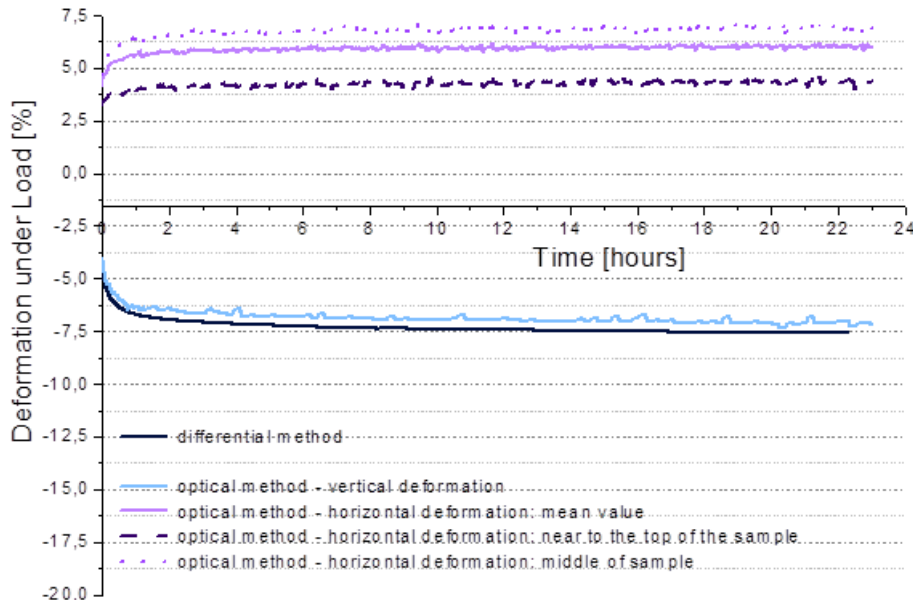


Fig. 34: Creep in compression measurement of SiC containing refractory castable at 1500 °C in oxidising atmosphere and an initial stress of 0,6 MPa.

The creep rates of SiC containing refractory castable in different directions and even at different positions were also assessed for the first time (Tab. 9). In the vertical direction, i.e. direction of the applied load, both methods (differential and optical) gave comparable results. In the horizontal direction, small differences between the creep rates as measured by the different methods were assessed. Even though measurements of small creep rates are difficult to assess with high reliability, the determined creep rates were found to be coherent with 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 tend to assume progressively a barrel shape.

Tab. 9: Creep rates (%·h⁻¹) of SiC containing refractory castable in quasi steady state (“secondary creep”) at 1500 °C in oxidising atmosphere and an initial stress of 0,6 MPa.

Differential method	Optical method			
	Vertical deformation (loading direction)	Mean value	Near to the top of the sample	In the middle of the sample
0,0116	0,0125	0,0042	0,0038	0,0050

5. Modelling

5.1. Analytical models

Besides the investigation of refractory products for the glass industry, the project partner CRIBC was largely involved in the improvement and development of analytical models to describe the creep behaviour of refractory products at high temperature. Description of the models developed by the CRIBC within the framework of the CreepRef project can be found in their project final report and in the following publications:

- [12] Pilate P, Lardot V, Cambier F, Brochen E. Characterization of the Compressive Creep Behavior of Clay Refractory Materials, According to EN 993-9 and ISO 3187 standards. Development of a Viscoelastic Model, Proceedings of 57th international colloquium on refractories, (2014) 150-154
- [13] Pilate P, Lardot V, Cambier F, Brochen E. Contribution to the understanding of the high temperature behavior and of the compressive creep behavior of silica refractory materials, Journal of the European Ceramic Society 35 (2015) 813–822

5.2. Phenomenological model

Based on the results from exemplary studies of the SiC containing castable, Forschungsgemeinschaft Feuerfest e.V. set up a phenomenological model to describe the creep behaviour of refractory products.

At least three mechanisms, mutually influencing each other, were found to govern the creep behaviour of refractory systems under compressive stress:

- Arrangement of the coarse and medium grains, which form the skeleton of the system able to sustain the stress,
- Grain boundary sliding and viscous flowing of the intergranular phase,
- Pressure sintering which causes the rearrangement and densification of the system.

An effective initial packing (compact arrangement) for a refractory product offers little potential for deformation through microstructural rearrangement and is expected to hamper its creep tendency.

As soon as enough viscous phase is formed, grain boundary sliding and especially the viscous flowing of the intergranular phase lead to the primary (unsteady) creep of the system, which basically corresponds to the pressure sintering of the refractory system. As far as possible, a microstructural rearrangement takes place until reaching an equilibrium (quasi steady state) between the coefficient of friction of the refractory granular stacking and flow driving forces (i.e. the external pressure onto the system during creep testing). The viscous intergranular phase acts as lubricant fluid, which promotes the creep. The amount of viscous phase and its capacity to wet the grains is thought to be a decisive factor.

Further creep processes are therefore controlled by the capacity of the system to further rearrange itself with the rate at which the grain boundary slides and the viscous intergranular

phase flows for a given temperature. Thereby not only the temperature plays a role, but also the applied pressure and the atmosphere promote or impede the primary creep and eventually influence the creep rates in quasi steady state.

Finally, spatial limitations may not be neglected. They are expected to cause the gradient of vertical deformations observed between the extremity of the sample (top and the bottom) and the middle of the sample, which is free to expand in case of uniaxial compression such as described in the standards. Obviously if the system is not able to densify anymore, deformations take place where the material is free to expand. The deformation may once again largely depend on the coefficient of friction and cohesion forces of the refractory granular stacking.

Especially for the simulation of the behaviour of refractory lining from complex industrial system, for which many spatial limitations exist, results from one dimensional measurement should only be used with care. Information on the deformation in a second dimension, as provided by the optical dilatometer of the experimental testing device, are decisive for the development and validation of complex creep models and greatly improve the accuracy of complex numerical simulations.

6. Conclusion

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

The equipment developed within the framework of this project coupled with microstructural examinations was proven to be powerful combination for a comprehensive investigation of the creep behaviour of refractory products.

Along with project-specific development and improvements of testing equipment, the proficiency of the testing equipment was verified with measurements on reference materials and by comparison with standard testing equipment. Thanks to a system to control the atmosphere, the creep behaviour of carbon containing refractories, especially used in steel making applications, as well as other materials sensitive to oxidation such as SiC can now be characterised. An exemplary study of the creep behaviour and the reasons for the behaviour of SiC containing castable was performed.

The deformation levels at the end of the primary creep regime of the investigated SiC containing castable were found to be higher with increasing temperature and higher initial stress. In contrast, the creep rates in the quasi steady state appeared to be highly dependent of the microstructure obtained after the primary creep regime. High temperature and high initial stress conducted to important densification during the primary creep regime which impeded further creep process in oxidising atmosphere. In inert atmosphere, however, a much looser microstructure was achieved after the primary creep regime, and a relatively high creep rate after 12 hours was observed. The evolution of the refractory microstructure at elevated temperature was thus found to impact the creep behaviour. In addition, the obtained results highlight the necessity of smart control of the atmosphere in combustion plants using SiC containing castables.

Finally, the optical dilatometer provided insight and new information about the two-dimensional creep behaviour of refractory product. This information is provided for the first time and should be decisive to support the development and verification of 3-dimensional models.

7. References

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- [13] Pilate P, Lardot V, Cambier F, Brochen E. Contribution to the understanding of the high temperature behavior and of the compressive creep behavior of silica refractory materials, Journal of the European Ceramic Society 35 (2015) 813–822