

Testing of thermal shock resistance of nonoxide refractories

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1. Abstract

Refractory materials in all industries have gone through considerable progress in the last years. Lifetime and reliability of refractories have increased. In many fields such as waste incineration plants, carbon containing refractories are commonly used.

For the further improvement of these materials, the understanding of thermal shock resistance is one of the key issues. Yet, for the thermal shock testing, resistance of carbon containing refractories the oxidation of carbon at temperatures higher than 600 °C is a major issue. This paper describes an effective method to heat up carbon containing specimen for the main thermal shock testing methods e.g. the Hasselman method or thermal fatigue, allowing thermal shocks of more than 1200 K.

2. Thermal shock resistance and thermal fatigue in Refractories

The thermal shock resistance influences the failure of the refractories especially in cyclic processes [1]. Thermal shock resistance (TSR) is one of the major influencing parameters of refractories lifetime. Thermal shock resistance quantifies a ceramics ability to resist abrupt temperature changes and includes both, sudden cooling and sudden heating. When highly sensitive to sudden temperature changes, the matrix of the refractory will be destroyed even without mechanical influence due to thermal stress.

Thermal stress is the consequence, either because thermal expansion of a refractory is not possible due to constructive parameters, or because the thermal conductivity is insufficient, which leads to thermal gradient in the material itself. Both mechanisms will lead to cracks. In opposite to metals, which react with small plastic deformation, ceramic materials are subject to cracks, when exposed to sudden temperature changes. The resistance against thermal down shock is defined by the maximum heating rate, heat flow and temperature gradient without any crack initiation.

2.1 Thermal stress Parameters

Thermal stress generally depends on the materials thermal expansion, the Young's modulus, thermal conductivity but also on the geometry of the material and on thermal boundary conditions. The mineral phase composition influences the thermal conductivity, which – when high enough – avoids the occurrence of thermal stress by providing low thermal gradients. The structure of ceramics takes influence on pore size and pore size distribution. The presence of a certain porosity is essential, as pores are able to prevent cracks from growing. Generally, failure occurs, when the stress intensity K_I reaches the fracture toughness K_{IC} .

For this case, when assumed that the surface has T_1 and the core still T_0 , thermal stress can be calculated to:

$$\sigma_{th} = \frac{\alpha * E}{1 - \mu} (T_0 - T_1)$$

with: α = thermal expansion

E = Young's Modulus

μ = Poisson number

Failure induced by thermal stress occurs when the thermal stress reaches a critical value σ_c , or when the stress intensity factor K_I reaches the fracture toughness K_{IC} . According to Equation 2, the critical temperature difference to expect failure, is defined as R and is calculated to:

$$\Delta T_{(max)} = \frac{\sigma_c(1-\nu)}{\alpha * E} = R$$

R , the so called thermal stress parameter, is a constant of the material, defining the ability to resist crack initiation by thermal stress. Many factors, such as thermal conductivity λ , thermal heat transfer α , and the fracture toughness K_{IC} influence "R". When $R_{increases}$, the thermal shock resistivity will increase as well.

In reality, R describes thermal shock resistance under fast heat transfer conditions, e.g. water quench. Therefore it is the thermal expansion coefficient that normally decides thermal shock resistance of most ceramics. In practice, the heat transfer rate is not infinite and the heat transfer coefficient h [W/K m²] also controls the thermal stress development. Therefore the above "idealistic" equation is modified to include the conditions of heat transfer and conduction. Accordingly, under finite (slow) heat transfer conditions, the thermal shock parameter is defined rather as

$\Delta T_c = R' = k R$, including thermal conductivity " λ " effect on thermal shock:

$$R'_s = \frac{\lambda \sigma_c(1-\nu)}{\alpha * E} = \lambda R_s$$

with a maximum temperature difference of

$$\Delta T = AR' / h$$

The maximum stress allowed can be used to define a further thermal shock parameter, including the materials density and its heat capacity.

$$R'' = \frac{(1-\nu)\lambda\sigma_c}{\alpha E \rho C_p} = \frac{R'}{\rho C_p} = \frac{R \lambda}{\rho C_p}$$

The parameters R , R' and R'' describe the beginning of a crack. In many applications, the onset of cracks may be of advantage, e.g. those insulating materials which are not under mechanical load. Often, the limitation of crack extension may be more important. Because crack extension decreases with increasing initial crack size, materials with large initial cracks will have good thermal shock properties as long as no mechanical load is present.

Hasselman suggested a parameter for the resistance to thermal shock damage, R'''' . This parameter was formulated especially for those ceramics with high strength and short cracks.

$$R'''' = \frac{E^* \gamma_{WOF}}{\sigma_{f2}}$$

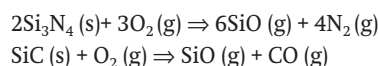
All "R" parameters include material properties, which are assumed to be independent of temperature. This assumption is not fulfilled in reality – besides that a size effect is not regarded - thermal shock parameters therefore can only give an estimation of thermal shock resistivity.

3. Testing Carbon Containing Specimen at high temperature

3. 1 Oxidation of carbon containing refractories

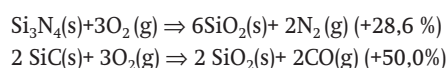
Carbon in refractories is mostly found as graphite or as SiC, which both are subject to oxidizing processes at higher temperatures, which is a key problem for the heating process in high temperature refractories testing.

Focusing on oxidation processes, principally, two kinds of oxidation have to be distinguished, the active and the passive oxidation. The active oxidation leads to a complete loss of the reaction products, leading to a loss of volume. Typical examples are the active oxidation of Si₃N₄ or SiC at low oxygen partial pressure. Both components oxidize to gaseous components:



The active oxidation has a linear coherence between loss of volume and the reaction time.

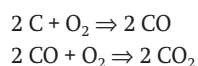
During the passive oxidation, solid oxidation products are formed on the surface of the oxidizing material, preventing the non-oxidic material from further oxidation and wear. This protective layer increases with ongoing reaction time at temperatures above 1200 °C [1]. The kinetic of oxidation is diffusion controlled [4]. The passive oxidation of the same materials leads to a gain of mass and volume:



To distinguish between active or passive oxidation, mostly the criteria of gain or loss of weight is chosen. The partial pressures of the gaseous phases O, SiO and CO at the interface of the material and the protective layer determine active or passive oxidation [5].

The materials of interest in this paper also contained graphite, mentioned as free carbon. As carbon oxidizes with the presence of oxygen at temperatures above 400 °C, the oxidizing process will weaken the structure of the refractory.

Free Carbon itself oxidizes according to the following equation:



In addition, the tested specimen contain SiC. SiC is inert against reducing gases such as CO or Nitrogen for up to 2000 °C. Oxygen, Air, CO₂ however oxidize SiC at temperatures higher than 800 °C, especially in the temperature interval of 1000 °C to 1200 °C to SiO₂ and CO₂. At temperatures higher than 1200 °C, SiO₂ forms a self protecting glaze on the SiC grains, slowing down further oxidation [3].

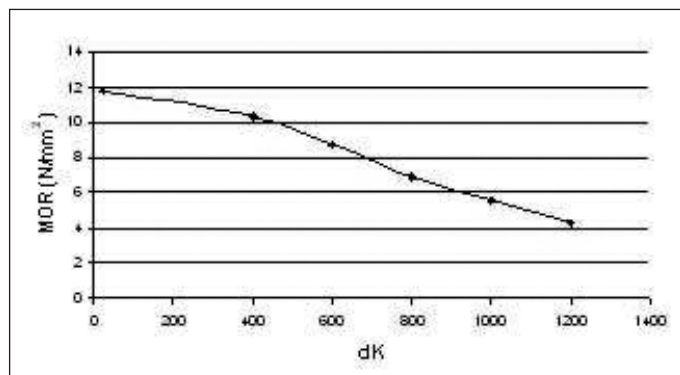


Fig. 1a and 1b. Hasselman results of an alumina and alumina mullite refractory

4. Experimentals

4.1 Measurement of thermal shock resistance and thermal fatigue

For the testing of the remaining bending strength of refractory specimen after thermal shock, two standard testing methods are available. Either, samples are heated up to 400 °C, 600 °C, 800 °C, 1000 °C etc and quenched in water. This is a method, proposed by Hasselman. The other method is to quench heated samples several times, and thereby determine their thermal fatigue. In both methods, after quenching, the specimen will be tested by a standard 3 point bending test. The Hasselman method leads to information on the remaining bending strength depending on the thermal shock by plotting the remaining bending strength versus the temperature difference. The following graphics show typical Hasselman results of alumina and of alumina-mullite material for refractories. Pure Alumina shows up to have constant remaining strength up to a critical temperature and then drops towards lower values. Alumina-mullite shows a constant decrease of the values, see **Figure 1**.

In the experimental part of the present paper, two carbon containing specimen were heated up to 1200 °C. After heating and quenching in water, the remaining bending strength was tested.

4.2 Specimen

As specimen for the experimental part, bars of two different qualities of carbon containing refractories were used. The major compositions of the specimen are according to **Table 1**. Both qualities contain carbon in the form of SiC and as graphite. **Figure 2** shows the prepared presmastic samples for cold bending tests after quenching.

4.3 Set up of an oxygen free furnace atmosphere

For an oxygen free kiln atmosphere, two demands have to be put into consideration: a kiln with a firing chamber which can be purged continuously with an inert gas during the heating process,

Tab. 1. Chemical composition in wt-% and Loss of Ignition (LOI) of specimen

	WZR 1	WZR 2
Al ₂ O ₃	7.0–12.0	7.0–11.0
Si	2.0–6.0	2.0–6.0
SiC	25.0–32.0	24.0–32.0
SiO ₂	15.0–24.0	15.0–23.0
Free Carbon	30.0–38.0	30.0–38.0
Fe ₂ O ₃	≈ 1	≈ 1
TiO ₂	≈ 1	≈ 1
Bulk Density (g/cm ³)	2.2–2.35	2.2–2.3
LOI (1000 °C; 2 h)	34.0–36.0	30–38



Fig. 2. Specimen of Carbon Containing Refractories



Fig. 4. Actual furnace

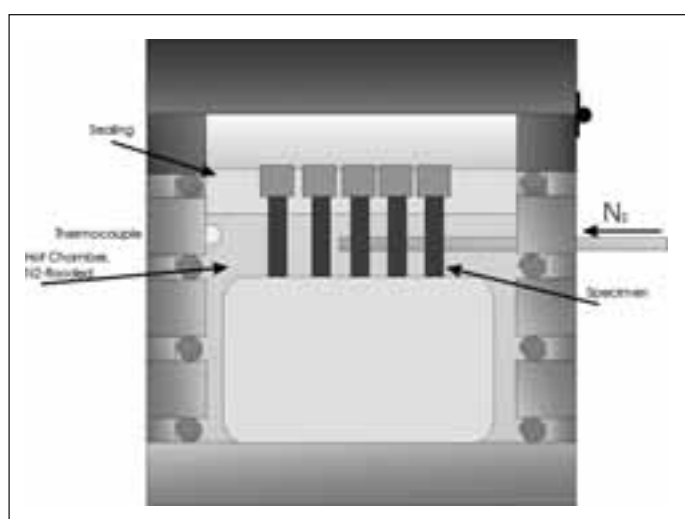


Fig. 3. Cross Section through the testing furnace

and a kiln, allowing specimen handling during operation without loss of inert atmosphere.

To achieve an oxygen free atmosphere, nitrogen was used as inert gas, in which graphite containing specimen are placed during the heating process. For the purpose of heating and testing graphite containing specimen, a top loading kiln has been modified and successfully tested, **Figure 4**. It allows handling specimen, while an N_2 atmosphere by purging into the firing chamber stays stable. Nevertheless, optimization and modification of a standard top loader kiln is necessary, especially focusing on tightening all openings in order to prevent oxygen from entering the chamber.

Through one of the two side openings of the furnace, a nitrogen supply was installed. The supply itself consisted of a nitrogen bottle and standard equipment to regulate the gas flow. The connection

into the furnace was achieved by a corundum tube, leading into the center of the firing chamber.

4.4 Furnace Sealing Design for testing

Figure 3–5 show the customized furnace sealing design. The chosen design insulates the kiln chamber from oxygen (air), and allows charging and removing of specimen during operation. According to their normed dimensions, the specimen were located on a block and were placed under single openings. These openings allow handling each specimen separately. Due to the temperature gradient between kiln chamber and surrounding air, an outward nitrogen stream prevents air from entering the kiln during handling.

4.5 Testing procedures

The chosen experimental setup was tested preliminary to define the current nitrogen flow. In first trials several specimen of graphite powder were heated up to $1000\text{ }^\circ\text{C}$, using a nitrogen flow of 30 l/h . To quantify especially the active oxidation process, the amount of powder was weighted before the heating and afterwards. After improvement of the whole construction and a higher nitrogen flow-rate of 150 l/h , the weight loss of graphite during the heating process could be eliminated, **Table 2**.

In a second pre-trial, the actual graphite containing specimens were tested. The samples were heated up under previously described conditions. Each specimen was quenched in water, dried at $110\text{ }^\circ\text{C}$ and recharged into the furnace. For determination of oxidation, each specimen was weighted before and after the test, as the weight loss is an indicator for active oxidation. It showed up to be essential to minimize the time between removal of the specimen from the oxygen free furnace atmosphere and the dipping into the water bath for quenching. During preliminary testing, the prismatic samples showed a weight reduction of app. 2% after five cycles of up heating, removing, quenching and again up heating. Due to the

Tab. 2. Oxidation of graphite powder in used furnace acc. to nitrogen flow

Sample	weight of Crucible	total weight before firing	T (furnace) $^\circ\text{C}$	N-flow (l/h)	total weight after firing	Weight loss in %
1	14.84	34.84	1000	30	31.87	8.5
2	14.75	34.75	1000	30	32.1	7.6
3	14.84	34.84	1000	60	31.47	6.8
4	14.75	34.75	1000	60	32.35	6.9
5	14.84	34.84	1000	130	34.1	2.1
6	14.75	34.75	1000	150	34.08	1.9
7	14.84	34.84	1000	150	34.80	0.1
8	14.75	34.75	1000	150	34.68	0.2

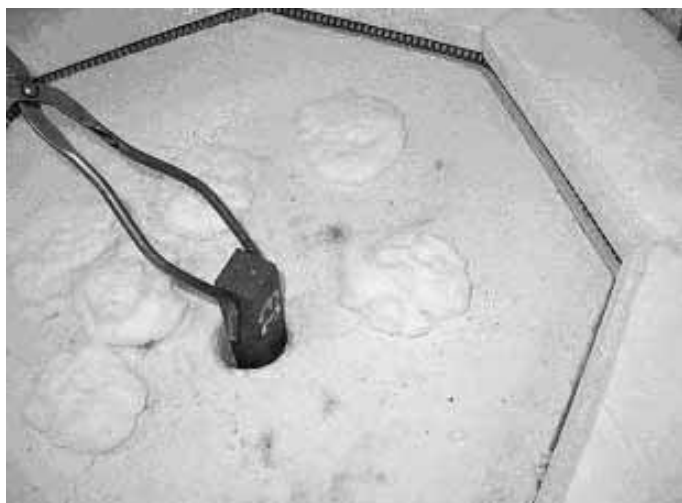


Fig. 5. Specimen during Charging

porosity of the material of 8–11 %, the quenching water bursted out small particles of the samples, which were found in the water bath after quenching. When the preliminary testing was focused to oxidation only – without water quenching – weight reduction was down to 0,5%. This value seemed to be considerably good for applying the testing method to graphite containing materials.

5 Results

5.1 Thermal shock resistance (Hasselmann)

The following two figures show the result of the Hasselmann testing method. All specimens have been quenched one time at the given temperature. Before testing their remaining bending strength

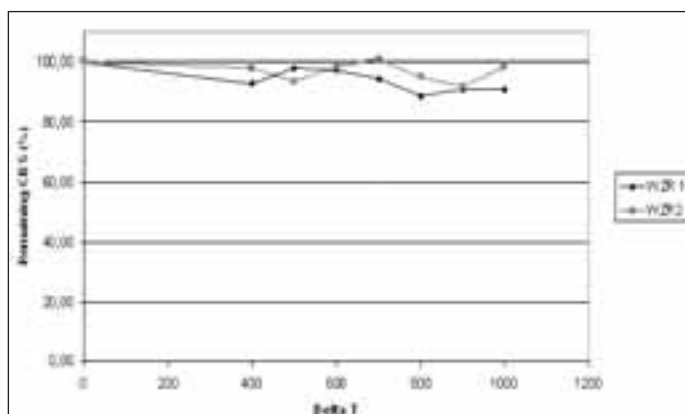


Fig. 6. Thermal shock resistance acc. Hasselmann

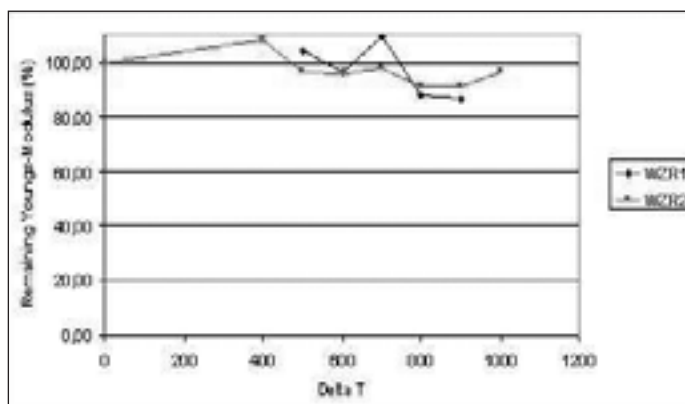


Fig. 7. Remaining Young's Modulus in (%)

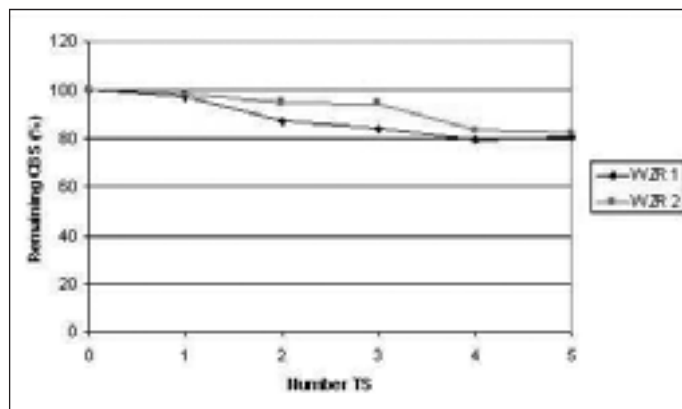


Fig. 8. Thermal Fatigue

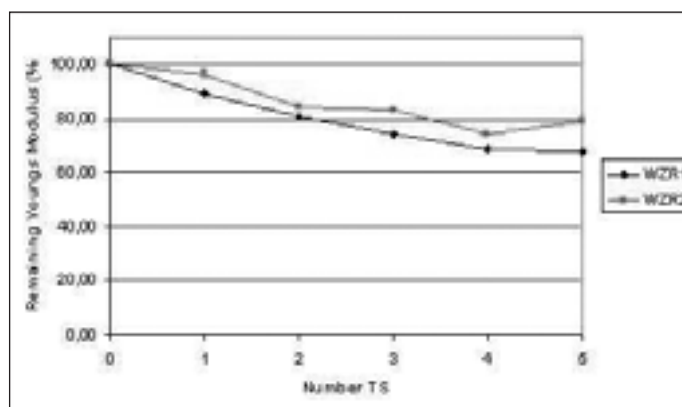


Fig. 9. Remaining Young's Modulus in thermal fatigue testing

(CBS), the young's modulus after quenching was measured, **Figure 6** and **7**.

Obviously, the remaining bending strength after up to 1000K is not reduced significantly. The Young's modulus remains at all temperatures around 100%, meaning that no structural degradation e.g. by oxidation has taken place. As mentioned before, the loss of weight is not significant for the chosen specimen due to their porosity and coarse grain sizes causing bursting effects during quenching.

5.2 Thermal fatigue

The specimen for thermal fatigue testing did the same testing procedure. Both qualities show a decrease in their remaining bending strengths to app. 80% of the initial strength. It is significant that also the remaining young's Modulus of these samples shows a constant decrease. Obviously, a degradation of the specimen's structure takes place. Whether this degradation is caused by thermal fatigue or by other effects basing on the specimens coarse grain sizes and porosity can only be determined after more testing of comparable samples with lower porosity, **Figure 8** and **9**.

6. Conclusions

The focus of the presented work was to determine how to set up a reproducible heating method for carbon containing refractories materials. The heating and hot testing of carbon containing materials need an oxygen free atmosphere in the used kiln. To prevent oxygen from oxidizing the samples by entering the firing chamber, it may be purged out by an overflow of neutralizing gas, such as nitrogen or argon. To achieve a stable oxygen free atmosphere even during opening the kiln for specimen removal or charging, a top loading kiln with modified power supply, continuous gas flow in-

serts and improved sealing showed up to be an easy manageable and yet reliable solution. The main advantage of this method is in the high quenching effects, realized by quenching the samples with water. Temperature drops of up to 1000K may be realized.

In further steps, two points need improvement. First point is the time of specimen removal from the kiln until their dipping into water. This step, which shortly exposes the heated samples to air causes some oxidation of the material. Improved handling of the specimen, keeping them under nitrogen flow may eliminate this.

The second point is the following cold bending test. In order to determine R'''' , the work of fracture need to be measured. This may be done by measuring the crack mouth opening displacement (CMOD) [3].

(F 52)

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