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BRITISH STANDARD

BS EN
12698-1:2007

Chemical analysis of nitride bonded silicon carbide refractories —

Part 1: Chemical methods

The European Standard EN 12698-1:2007 has the status of a British Standard

ICS 71.040.40

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National foreword

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A list of organizations represented on this committee can be obtained on request to its secretary.

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EUROPEAN STANDARD

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Chemical analysis of nitride bonded silicon carbide refractories - Part 1: Chemical methods

Analyse chimique des produits réfractaires contenant du carbure de silicium à liaison nitrure - Partie 1: Méthodes chimiques

Chemische Analyse von feuerfesten Erzeugnissen aus nitridgebundenem Siliciumcarbid - Teil 1: Chemische Verfahren

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Foreword

This document (EN 12698-1:2007) has been prepared by Technical Committee CEN/TC 187 “Refractory products and materials”, the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2007, and conflicting national standards shall be withdrawn at the latest by September 2007.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

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1 Scope

This standard describes the methods for the analysis of all refractory products containing nitride and oxynitride bonded silicon carbide, irrespective of the silicon carbide level. It includes details of sample preparation, general principles of chemical analysis and detailed methods for the determination of carbon, silicon carbide, free aluminium, free silicon, total nitrogen and oxygen.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 12475-4:1998, *Classification of dense shaped refractory products — Part:4 Special products*

EN 12698-2, *Chemical analysis of nitride bonded silicon carbide refractories — Part 2: XRD methods*

prEN ISO 21068, *Chemical analysis of silicon carbide containing raw materials and refractory products*

ISO 836:2001, *Terminology for refractories*

ISO 3310-1*, Test sieves — Technical requirements and testing — Part 1: Test sieves of metal wire cloth*

ISO 5022*, Shaped refractory products — Sampling and acceptance testing*

ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 8656-1, *Refractory products — Sampling of raw materials and unshaped products — Part 1: Sampling scheme*

3 Terms and Definitions

For the purposes of this document the terms and definitions given in ISO 836:2001, EN 12475-4:1998 and the following apply.

3.1
nitride and oxynitride bonded silicon carbide refractories
refractory products predominantly consisting of silicon carbide with minor amounts of nitride phases as a matrix component

NOTE In general, metallic silicon is used as precursor material which undergoes a phase transformation in an oxygen-free nitrogen atmosphere.

4 Methods for determination

A list of methods and the relevant European Standards are given in Table 1.

Carbon is determined by the evolution of carbon dioxide on combustion in a stream of oxygen at defined temperatures. Silicon carbide is calculated by the difference of total carbon (C_{total}) and free carbon (C_{free}).

NOTE 1 The carbon dioxide evolved can be conveniently measured coulometrically, gravimetrically by absorbtion onto soda lime, or by infrared detection.

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Free aluminium is determined by the evolution of hydrogen on treatment with hydrochloric acid and by measuring the gas volume in a nitrometer. Free silicon shall be determined on the same sample by treatment with sodium hydroxide.

Total nitrogen is determined by a variety of methods: carrier gas fusion, alkaline fusion, Kjeldal distillation or microwave digestion.

NOTE 2 The nitrogen can be conveniently measured by thermal conductivity or after digestion as ammonium by titration with hydrochloric acid.

Distinction between aluminium nitride and silicon nitride is made by their reaction with sodium hydroxide solution; aluminium nitride is quantitatively decomposed yielding free ammonia, while silicon nitride is unaffected.

A convenient commercial apparatus for determining total oxygen consists of an induction furnace in which the sample is heated with pure carbon. Carbon dioxide and carbon monoxide are measured by infrared absorption and the integrated signals are combined to give the total oxygen content.

NOTE 3 Specification of many of the constituents can often be made using XRD techniques, e.g. free silicon, silicon nitride, silicon oxynitride, quartz and cristobalite (see EN 12698-2).

Table 1 — Methods and relevant European Standards

Item tested	European Standard
Carbon and silicon carbide	prEN ISO 21068
Free silicon	prEN ISO 21068
Oxygen	prEN ISO 21068
Free aluminium	EN 12698-1
Total nitrogen	EN 12698-1
Silicon nitride/oxynitride, free silica	EN 12698-1
XRD	prEN ISO 21068 and EN 12698-2
Sialon	EN 12698-2
Free carbon	prEN ISO 21068 or EN 12698-1
Total carbon	prEN ISO 21068
Silicon carbide	prEN ISO 21068 and EN 12698-1
Free alumina	EN 12698-1

5 Sampling

Sample shaped and unshaped products using the procedures given in ISO 5022 and ISO 8656-1.

When sampling large fragments, take care to collect samples from different points of individual pieces.

Homogenize the sample by reducing the maximum particle size to 150 µm and take the test sample from this material.

6 Determination of free aluminium

6.1 Principle

The volume of hydrogen generated by the action of dilute hydrochloric acid on any free aluminium in a sample is measured.

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If the sample is known to contain carbonate, then the volume of hydrogen evolved is corrected for the known carbonate content.

The free aluminium content can also be determined by the evolution of hydrogen using sodium hydroxide. In this case, the volume of hydrogen evolved is corrected for the silicon content. Free iron will also evolve hydrogen; a correction is made for the iron content.

6.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade

6.2.1 Distilled water or water which has been fully demineralized by ion exchange (deionized water) and reagents of analytical grade.

6.2.2 Dilute hydrochloric acid, 1+1 by volume.

6.3 Apparatus

6.3.1 Nitrometer, as used for determining free silicon.

6.3.2 Balance, capable of reading to the nearest 0,1 mg.

6.4 Sample preparation

Dry the test sample (sampling as described in clause 5) a to constant mass at (110 ± 10) °C for a minimum of 2 h prior to analysis.

6.5 Procedure

Weigh (0,5 ± 0,01) g of sample into a clean, dry nitrometer tube. Place a dry ignition tube inside the tube and holding the nitrometer tube upright, introduce, using a long dropping pipette and without letting any touch the sample, 5 ml of dilute hydrochloric acid into the ignition tube.

Carefully fit the bung of the apparatus making sure there is good seal. Equalize the pressure and leave the three-way tap in a position that connects the sample and graduated tube. Tip the acid out of the ignition tube onto the sample. Shake the apparatus gently and allow it to stand for 15 min. Read off the volume after equalizing the pressure. Shake gently and read again after another 5 min to 10 min. Record the final volume reading when consecutive readings are the same. Also note the temperature and barometric pressure.

NOTE If this method is used frequently, it is recommended that a conical flask with airtight sample insert device, e.g. a side-on positioned ground-in connection and ground-in stopper with weighing bottle (special version) is used. The weighed sample is placed into the stopper-connected weighing bottle. The hydrochloric acid is added to the flask. After equalizing the pressure, the sample powder is added to the acid by turning the stopper.

6.6 Calculation and expression of results

Correct the volume reading to the gas volume at standard temperature, $V_{(STP)}$ in ml, using equation (1):

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$$V_{(\mathrm{STP})} = V_1 \times \frac{\left(p - p_{\mathrm{H_2O}}\right)}{1\,013{,}25} \times \frac{273}{\left(273 + T\right)} \quad (1)$$

where

V_1 is the measured volume, in ml;

p is the atmospheric pressure, at time of measurement, in hPa;

$p_{\mathrm{H_2O}}$ is the partial pressure of water vapour at the measured temperature, in hPa;

T is the measured temperature, in °C.

Calculate the percentage of free aluminium, A, using equation (2):

$$A = V_{(\mathrm{STP})} \times 0{,}000\,804 \times \frac{100}{m} \quad (2)$$

where

m is the mass of the sample, in g.

Report the result to the nearest 0,1 %.

7 Determination of total nitrogen

7.1 General

To determine total nitrogen one of the four methods given in 7.2 to 7.5 shall be used.

7.2 Determination of total nitrogen by carrier gas fusion (CGF)

7.2.1 General

This method is used to determine nitrogen in silicon nitride, Si_3N_4, and other compounds, in the form of nitrides and oxynitrides by thermal decomposition.

7.2.2 Principle

A sample, prepared as described in clause 5, is decomposed in a graphite crucible in a stream of carrier gas (helium) by heating it to above 2 400 °C in a resistance furnace (electrode furnace).

The gases released are mainly nitrogen, carbon monoxide and hydrogen. The carbon monoxide and hydrogen are oxidized to carbon dioxide and water and then removed by absorption. Alternatively, formed carbon monoxide and gases other than nitrogen shall be removed, for example, using a molecular sieve. The change in thermal conductivity due to the nitrogen component is then measured.

The details of the determination procedure can vary with the type of apparatus used and it is therefore only possible to give general instructions that can be used with any type of apparatus. Using the gas calibration, the validity of the results is confirmed by analysing a reference material having similar extraction behaviour.

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7.2.3 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade.

7.2.3.1 Distilled water, or water which has been fully demineralized by ion exchange (deionized water).

7.2.3.2 Helium, having a minimum purity of 99,99 %.

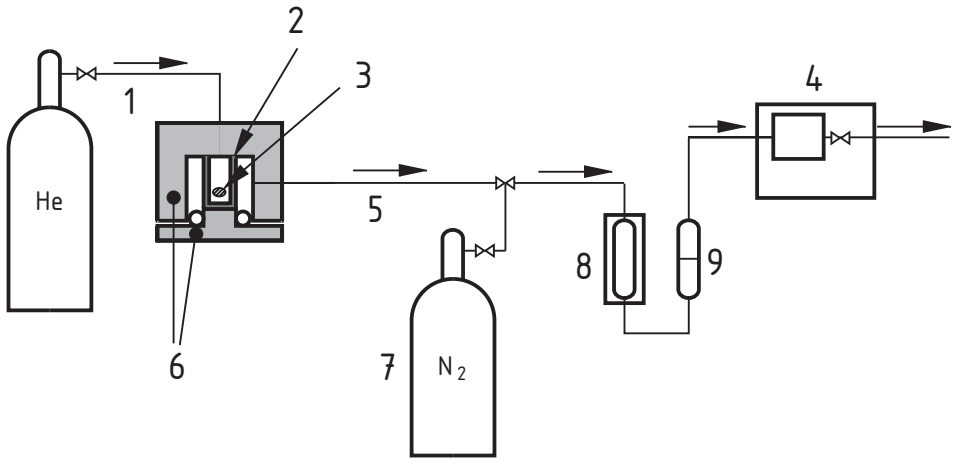
7.2.3.3 Nitrogen, having a minimum of 99,99 %.

7.2.3.4 Catalysts, such as copper oxide.

7.2.3.5 Sorption agents for removing water vapour and carbon dioxide, e.g. magnesium perchlorate, sodium hydroxide on a support, or a molecular sieve.

7.2.4 Apparatus

7.2.4.1 Measurement device, commercially available apparatus consisting of a resistance furnace and a measuring unit for determining nitrogen in a stream of carrier gas using a thermal conductivity cell. An example of a suitable apparatus is given in Figure 1.



Key

1. Carrier gas
2. Crucible
3. Sample
4. Thermal conductivity cell
5. He plus gases from sample
6. Electrodes
7. Calibration gas
8. Apparatus for oxidizing carbon monoxide and hydrogen ($CO \rightarrow CO_2$; $H_2 \rightarrow H_2O$)
9. Carbon dioxide and water vapour absorption tubes ($H_2O\downarrow$ $CO_2\downarrow$)

Figure 1 — Gas flow diagram for the determination of total nitrogen by carrier gas fusion

7.2.4.2 Analytical balance, capable of measuring to the nearest 0,01 mg.

7.2.4.3 Graphite crucibles, having approximately the same electrical resistance. The crucibles shall contain concentrations of nitrogen as low as possible. The nitrogen shall be removed by out-gassing, which can be proved by blank determinations.

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7.2.5 Sample preparation

Dry the test sample to constant mass at (110 ± 10) °C. It is advisable to encase the sample in tin, nickel or platinum and compress it so as little air as possible is included. Using bath metals such as casing materials (capsules or foil) will ensure formation of a homogeneous melt for the extraction.

NOTE The addition of bath metals, e.g. nickel or tin, may also be necessary to complete the extraction.

7.2.6 Procedure

The mass of the sample depends on the type of apparatus used, but the sample shall not be less than 4 mg.

The lower limit depends on the homogeneity of the sample material and the upper limit on the calibration range of the apparatus; the initial sample mass will depend on the anticipated nitrogen content.

Follow the manufacturer's operating instructions for the apparatus.

Place the crucible in the furnace and de-gas it at 100 °C above the analysis temperature. Weigh the sample and record its mass to the nearest 0,01 mg. Add the sample to the crucible and heat it.

NOTE Reliable analytical results will only be obtained if adequate information relating to sample preparation, procedure, calibration, recalibration and checking, and apparatus maintenance is available from in-house experiments and experience.

7.2.7 Calibration and recalibration

7.2.7.1 Gas calibration

Carry out gas calibration by adding a known amount of nitrogen gas. Calculate the amount of gas added, m in mg, using equation (3):

$$m = \frac{p \times V_{\mathrm{T}} \times \rho_{\mathrm{N_2}}}{p_{\mathrm{n}}\left(1 + \gamma \times T\right)} \tag{3}$$

where

p is the corrected barometric pressure, in hPa;
T is the temperature, in °C;
V_{T} is the gas volume added, in ml at T °C and p hPa;
ρ_{N2} is the density of nitrogen gas under standard conditions, i.e. 1,250 4 mg/ml;
γ is the cubic coefficient of thermal expansion of nitrogen (0,003 671 K^{-1});
p_{n} is the standard pressure, 1013,25 hPa.

The linearity of the evaluation curve is fixed by this procedure. This can also be done with a computer connected to the measuring equipment. The calibration, however, will not provide any information about the efficiency of the extraction process. This can only be determined by analysing suitable reference samples. The latter approach is the only one possible for systems not designed for gas calibration.

7.2.7.2 Calibration using solids

For calibration with solids, the reference material shall be analysed using widely varying sample masses covering as much as possible, the entire calibration range of the apparatus.

NOTE 1 The relative analytical error will increase if smaller sample masses are used.

NOTE 2 If linearity has been found beforehand by calibration using gas addition or a reference sample, any variation is the analytical result in connection with the initial sample mass and can be unambiguously ascribed to an inefficient extraction process.

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7.2.8 Checking and maintaining the apparatus

Before a new apparatus is used, the manufacturer's data on the measurement range, initial sample mass, reproducibility and stability shall be checked using suitable samples with known nitrogen contents. The manufacturer's instructions for regular checks and maintenance shall be carried out.

NOTE Incorrect results can be expected if replacement of the oxidation and sorption reagents it is not carried out in due time.

7.2.9 Calculation

Typically, using state of the art instrumentation, the nitrogen content is automatically calculated through the calibration function in % by mass by entering the sample mass. If only nitrogen mass is indicated, calculate the nitrogen content in % by mass manually.

For older instrumentation where only a measuring category for nitrogen is indicated, it is necessary to plot a calibration curve. The concentration of the test sample is calculated from the value of the calibration samples measured via the calibration curve.

7.2.10 Precision

Under the specified conditions, the values of the repeatability limit r, and the reproducibility limit R, as defined in ISO 5725-1 are:

r = 1 %;

R = 2 %.

NOTE An improved reproducibility and accuracy may be expected if certified reference materials are used for calibration.

7.3 Determination of total nitrogen content by fusion decomposition

7.3.1 General

This method is used to determine nitrogen in silicon nitride, Si_3N_4, and other compounds in the form of nitrides and oxynitrides by fusion decomposition. Analogous methods may be used to determine nitrogen in materials containing not less than 5 % by mass of nitrogen bound in the form of nitrides and oxynitrides.

7.3.2 Principle

The sample is fused with lithium hydroxide at no more than 700 °C to convert the nitrogen into ammonia. A gentle stream of inert gas is used to transfer the ammonia to a receiving vessel containing boric acid solution and the amount of nitrogen is determined by titration with an acid of known concentration.

7.3.3 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade.

7.3.3.1 Distilled water, or water which has been fully demineralized by ion exchange (deionized water).

7.3.3.2 Powdered lithium hydroxide, LiOH.

7.3.3.3 Sulfuric acid, ρ = 1,84 g/ml.

7.3.3.4 Standard solution, 0,1 mol/l hydrochloric or sulfuric acid of known standardization for titration.

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7.3.3.5 Boric acid solution, prepared by dissolving 40 g of boric acid, H_3BO_3, in 1 l of hot water.

7.3.3.6 Inert gas, argon or nitrogen (nitrogen acts as an inert gas for this reaction), with a purity of 99,99 % as inert gas.

7.3.3.7 Sodium carbonate, Na_2CO_3, 99,95 % to with a purity of at least 99,95 %.

7.3.3.8 Calcium chloride, $CaCl_2$, dried.

7.3.4 Apparatus

7.3.4.1 Analytical balance, capable of reading to the nearest 0,01 mg.

7.3.4.2 Measurement device, apparatus for releasing, carrying over and absorbing ammonia (see Figure 2), comprised of:

a) flow meter;

b) gas washing bottles;

c) vitreous silica reaction tube with ground joints, stoppers and gas inlet;

d) unglazed porcelain boats;

e) tubular furnace, e.g. heated by infrared radiation, capable of being heated to, and maintained at, (700 ± 10) °C;

f) vitreous silica wool;

g) gas inlet tube with ground joint and capillary tip;

h) absorption vessel.

In this apparatus, the inert gas from a pressurized gas cylinder passes through a gas washing bottle filled with sulfuric acid with a density, ρ = 1,84 g/ml, preceded and followed by an empty washing bottle for safety reasons.

NOTE 1 No gas purification is necessary if the ammonia content of the inert gas does not exceed 0,005 % by volume.

The inert gas is then passed through a flow meter and into the vitreous silica reaction tube at the side gas inlet. The ground joint through which the sample is inserted is also located at this point. The other end of the reaction tube is connected by a ground joint to a gas inlet tube whose tip has been drawn out to form a capillary and extends almost to the bottom of a narrow absorption vessel.

NOTE 2 The reaction tube can also be a gas-tight ceramic tube with the sample inlet and borosilicate glass ground joint shown in Figure 1, which are fused on or attached by means of silicone hoses.

The reaction tube shall be heated by a tubular furnace which can be maintained at (700 ± 10) °C. The still hot part of the tube outside the tubular furnace and adjacent to the absorption vessel is packed with loose vitreous silica wool which is capable of condensing any lithium hydroxide which evaporates.

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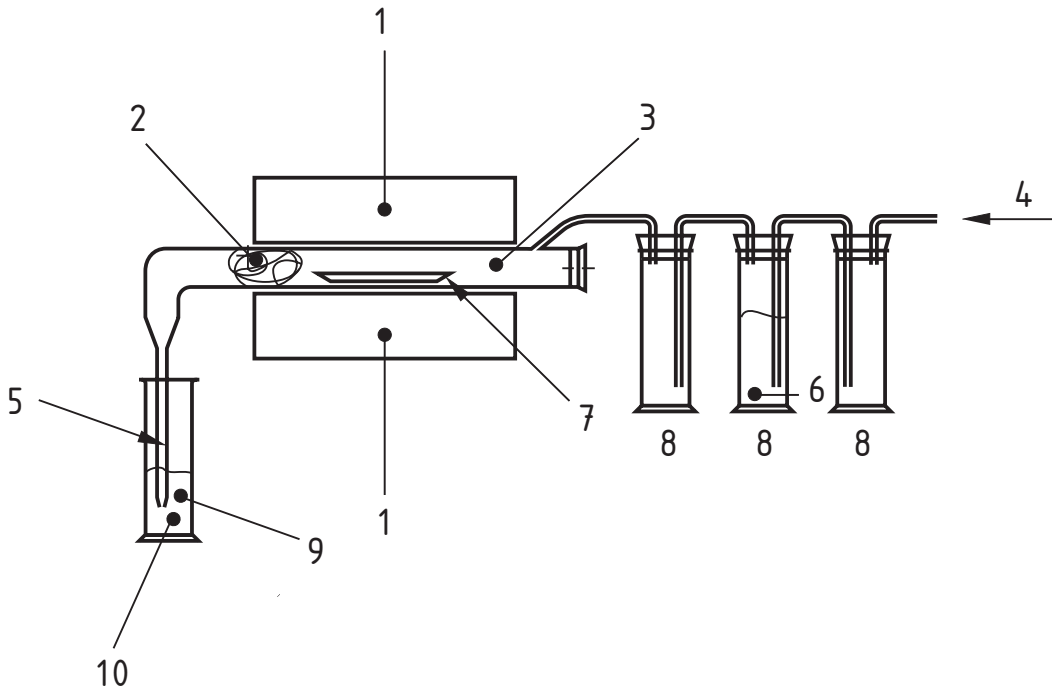

Key

1. Tubular furnace
2. Vitreous silica wool
3. Vitreous silica tube with connections
4. Inert gas
5. Gas inlet tube with capillary tip
6. Sulfuric acid
7. Porcelain boat
8. Washing bottles
9. Boric acid solution
10. Absorption vessel

Figure 2 — Nitrogen determination apparatus for fusion decomposition

7.3.4.3 Potentiometric titrator, with a metering volume of 50 ml and a maximum relative tolerance of 0,1 %.

7.3.5 Sample preparation

Dry the test sample (sampled as described in clause 5) to constant mass at (110 ± 10) °C for a minimum of 2 h prior to analysis.

7.3.6 Procedure

7.3.6.1 Decomposition by fusion

NOTE The time for complete reaction should be established before the method is applied.

Coat the entire inside of the porcelain boats with 500 mg of lithium hydroxide at 600 °C and store the boats in a desiccator. Weigh 100 mg of the sample to the nearest 0,01 mg, into a coated porcelain boat and mix thoroughly with 1,5 g of lithium hydroxide. Flush the apparatus with inert gas and pour 40 ml of boric acid solution into the absorption vessel and immerse the gas inlet tube in it. Set the inert gas flow to 70 normal ml/min to 100 normal ml/min, open the ground joint closure and push the porcelain boat into the centre of the reaction tube to the point where the thermocouple is located. After closing the tube again, slowly heat the tubular furnace to 700 °C in steps to prevent the melt from spattering. For tubular furnaces that heat up rapidly, the heating phase shall not be less than 15 min. After 30 min at (700 ± 10) °C, the nitride nitrogen will have been quantitatively converted into ammonia. Ensure the furnace temperature does not, under any circumstances exceed 730 °C, because the lithium hydroxide will start to evaporate above that temperature.

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7.3.6.2 Standardization of titration acid

Dry the sodium carbonate at 270 °C to 300 °C for 1 h, stirring occasionally, and store it in a desiccator over calcium chloride.

Weigh 200 mg of dried sodium carbonate to the nearest 0,01 mg in a sealable weighing bottle.

Dissolve the sodium carbonate in 50 ml of distilled water and add the titration acid to be standardized using a potentiometric titrator until the equivalent point in the pH range 4,6 ± 0,2 is reached. Take the mean value of not less than three titrations. The coefficient of variation shall not exceed 0,001.

7.3.6.3 Titrating the absorption solution

When the reaction is complete, remove the gas inlet tube from the absorption vessel and rinse its inside and outside with a few millilitres of water. Titrate the amount of absorbed ammonia to the equivalence point which is generally a pH value of 4,6 ± 0,2 with the standardized titration acid using the potentiometric titrator.

7.3.6.4 Blank value

Carry out a blank determination as described in 7.3.6.1 and 7.3.6.3, without a test sample.

7.3.7 Calculation and expression of results

7.3.7.1 General

When calculating the results, the acid titration factor (7.3.7.2) shall be included.

Report the result to the nearest 0,1 %.

7.3.7.2 Calculation of acid titration factor

Calculate the titration correction factor, t, of the acid using equation (4):

$$t = \frac{m_{\mathrm{Na}}}{5{,}2994 V_1} \tag{4}$$

where

m_{Na} is the sample mass of sodium carbonate, in mg;
V_1 is the volume used of the 0,1 mol/l acid to be standardized, in ml;
5,299 4 is the titrimetric factor, in mg/ml.

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7.3.7.3 Calculation of nitrogen content

Calculate the nitrogen content, M_N, as a percentage by mass using equation (5):

$$M_N = \frac{(V_2 - V_3) \times t \times 1{,}400\ 7 \times 100}{m} \quad (5)$$

where

V_2 is the volume of titration acid used for the sample, in ml;
V_3 is the volume of titration acid used for the blank value, in ml;
t is the titration correction factor of the acid;
m is the sample mass, in mg;
1,400 7 is the titrimetric factor, in mg/ml.

7.3.8 Precision

Under the specified conditions, the values of the repeatability limit r, and the reproducibility limit R, as defined in ISO 5725-1 are:

r = 0,5 %;

R = 0,9 %.

7.4 Determination of total nitrogen content by Kjeldahl distillation

7.4.1 Principle

The nitrogen in silicon nitride, Si_3N_4, and other compounds in the form of nitrides and oxynitrides method are determined using high pressure acid decomposition.

The sample is dissolved in hydrofluoric acid under pressure and the nitrogen is distilled over as ammonia into a receiving vessel containing boric acid solution, using an ammonia distillation apparatus. The Nitrogen content is determined by potentiometric titration.

7.4.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and of known analytical purity.

7.4.2.1 Distilled water, or water which has been fully demineralized by ion exchange (deionized water).

Unless otherwise specified, solutions are aqueous.

7.4.2.2 Hydrofluoric acid, HF, ρ = 1,13 g/ml.

7.4.2.3 Boric acid, H_3BO_3.

7.4.2.4 Boric acid solution, to be prepared by dissolving 40 g of boric acid in 1 l of hot water.

7.4.2.5 Sodium carbonate, Na_2CO_3, 99,95 % to 100,05 %.

7.4.2.6 Hydrochloric acid, or sulfuric acid solution, c(HCl) or c(H_2SO_4) = 0,1 mol/l or 0,05 mol/l.

7.4.2.7 Sodium hydroxide solution, to be prepared by dissolving 400 g of sodium hydroxide in 1 l of water.

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7.4.3 Apparatus

Ordinary laboratory apparatus and the following:

7.4.3.1 Analytical balance, capable of reading to the nearest 0,01 mg.

7.4.3.2 Laboratory oven or microwave oven, suitable for temperatures up to 230 °C.

7.4.3.3 Apparatus for the determination of ammonia, e.g. by the Parnas-Wagner method, with a steam generator.

7.4.3.4 Digestion apparatus to be used under pressure, with poly-tetrafluoroethylene inserts with a capacity of 100 ml and suitable for use at temperatures up to 200 °C.

7.4.3.5 Potentiometric titrator, comprised of a pH measuring cell and a metered volume of (50 ± 0,025) ml.

7.4.4 Sample preparation

Dry the test sample (sampled as described in clause 5) to constant mass at (110 ± 10) °C for a minimum of 2 h prior to analysis.

7.4.5 Procedure

7.4.5.1 Decomposition of sample under pressure

Weigh 500 mg of the test sample, pre-treated as specified in 7.4.4, to the nearest 0,01 mg. Transfer this quantitatively to the polytetrafluoroethylene insert of the pressurized digestion apparatus and add 5 ml of water and 10 ml of hydrofluoric acid. Seal the apparatus as directed by the manufacturer and heat. Ensure that the solution and sample are kept at (200 ± 5) °C for 4 h to 6 h. After cooling and opening the apparatus, bind the excess hydrofluoric acid by adding 4,7 g of boric acid. Ignore any dark particles which are occasionally left behind. Transfer the solution to a 250 ml volumetric flask and make up to the mark with water.

7.4.5.2 Standardization of titration acid

Weigh 200 mg of sodium carbonate to the nearest 0,01 mg into a sealable weighing bottle.

Dry the sodium carbonate at 270 °C to 300 °C for 1 h, stirring occasionally, and store it over calcium chloride in a desiccator.

Dissolve the sodium carbonate in 50 ml of water and add the titration acid using a potentiometric titrator apparatus until the equivalence point in the pH range of 4,1 to 4,3 is reached. Take the mean of not less than three titrations. The coefficient of variation shall not exceed 0,001.

7.4.5.3 Distillation and potentiometric titration

Use a one-mark bulb pipette to pipette a 50 ml aliquot portion of the solution prepared as described in 7.4.5.1 into an ammonia determination apparatus which has been steamed out. Pour 20 ml of boric acid solution into the receiving vessel of the still and immerse the condenser outlet in the solution. After adding 50 ml of sodium hydroxide solution to the digestion solution, distil over the ammonia into the receiving vessel by passing steam through the heated solution until 200 ml to 250 ml has been collected. The reaction is complete when there is no change in the pH value of the boric acid solution.

Determine the amount of ammonia absorbed by the boric acid solution by potentiometric titration using the standardized titration acid. The equivalence point is in the pH range of 4,6 ± 0,2.

NOTE The time for complete reaction should be established before the method is applied.

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7.4.5.4 Blank value

To determine the blank value, subject the amount of acid used for digestion to the analysis procedure described in 7.4.5.1 and 7.4.5.3.

7.4.6 Calculation and expression of results

7.4.6.1 General

For calculation of results the titration correction factor (7.4.6.2) shall be included.

Report the result to the nearest 0,1 %.

7.4.6.2 Calculation of the titration correction factor

Calculate the titration correction factor, t, of the acid using equation (4).

7.4.6.3 Calculation of nitrogen content

Calculate the nitrogen content, M_N, as a percentage by mass using equation (5).

7.4.7 Precision

Under the specified conditions, the values of the repeatability limit r, and the reproducibility limit R, as defined in ISO 5725-1 are:

r = 0,4 %;

R = 0,9 %.

NOTE The results are based on an inter-laboratory test carried out by Technical Committee *Sonderwerkstoffe des Chemikerausschusses der GDMB* (GDMB = German Foundry and Mining Society).

7.5 Determination of total nitrogen by microwave digestion

7.5.1 Principle

This method is used to determine nitrogen in silicon nitride, Si_3N_4 and other nitrides and oxynitrides using high pressure acid decomposition.

The sample is dissolved in hydrofluoric/ hydrochloric acid in a microwave device under pressure and the nitrogen is distilled over as ammonia into a receiving vessel containing boric acid solution, using an ammonia distillation apparatus, and determined by change in colour titration.

7.5.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and of known analytical purity.

7.5.2.1 Distilled water, or water which has been fully demineralized by ion exchange (deionized water).

7.5.2.2 Sodium hydroxide pellets.

7.5.2.3 Hydrofluoric acid 40 %, ρ = 1,13 g/ml.

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7.5.2.4 Hydrochloric acid, ρ = 1,19 g/ml.

7.5.2.5 Mixture of hydrofluoric acid (see 7.5.2.3) and hydrochloric acid (see 7.5.2.4), 1+1 by volume.

7.5.2.6 Sodium hydroxide solution, 4 mol/l.

7.5.2.7 Phenolphthalein indicator, 1 % in ethanol, m/m.

7.5.2.8 Hydrochloric acid, 0,1 mol/l.

7.5.2.9 Boric acid solution, saturated, approximately 5 %.

7.5.2.10 Mixed indicator solution, of 1 volume methyl red solution (0,1 % m/m in ethanol) and 5 volumes bromocresol green (0,1 % by mass in an ethanol/water mixture of 1+1 by volume).

7.5.3 Apparatus

Ordinary laboratory apparatus and the following.

7.5.3.1 Analytical balance, capable of reading to the nearest 0,01 mg.

7.5.3.2 Microwave digestion device.

7.5.3.3 Microwave digestion vessel to be used under pressure, with a capacity of 50 ml and suitable for temperatures up to 250 °C.

7.5.3.4 Apparatus for the determination of ammonia, e.g. by the Parnas-Wagner method, with a steam generator.

7.5.3.5 Burette, with a metered volume of (50 ± 0,025) ml.

7.5.4 Sample preparation

Dry the test sample (sampling as described in clause 5) to constant mass at (110 ± 10) °C for a minimum of 2 h prior to analysis.

7.5.5 Procedure

Weigh (0,5 ± 0,05) g of sample into a clean Teflon pressure vessel. In a fume cupboard, carefully add 5 ml of hydrofluoric acid/hydrochloric acid mixture (see 7.5.2.5) and swirl gently. Place a rupture membrane in position in the cap and secure the cap on the vessel as described in the manufacturer's microwave handbook. Place the vessel in the microwave oven, and select a suitable programme.

Allow the vessel to cool.

In a fume cupboard, cautiously vent, and remove the cap, rinsing well with distilled water. Add 10 ml of saturated boric acid solution (see 7.5.2.9) to the vessel.

Carefully wash out the acid solution from the vessel into a 250 ml flat-bottomed flask, with distilled water, making the volume up to 150 ml, add a few anti-bumping granules, a few drops of phenolphthalein and enough 4 M sodium hydroxide solution to produce an alkaline solution, (approximately 30 ml).

Connect the flask to the distillation apparatus. Place 100 ml of saturated boric acid and 5 drops of mixed indicator in the collection beaker and rise to dip the condenser in the boric acid. Place an electric burner

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under the distillation flask and boil until the volume is reduced to about half. Lower the collection beaker and remove the electric burner. Wash down the condenser with distilled water.

Titrate the solution obtained with 0,1 M hydrochloric acid until the colour changes from dark blue to the pink end point.

7.5.6 Calculation and expression of results

7.5.6.1 General

For calculating results the titration correction factor (7.5.6.2) shall be included.

Report the result to the nearest 0,1 %.

7.5.6.2 Calculation of the titration correction factor

Calculate the titration correction factor, t, of the acid using equation (4).

7.5.6.3 Calculation of nitrogen content

Calculate the nitrogen content, M_N, as a percentage by mass using equation (5).

7.5.7 Precision

See clause 7.4.7

NOTE Because of the similarity between the methods comparable precision may be assumed.

8 Determination of free silicon

Determine the free silicon using the hydrogen evolution method given in prEN ISO 21068.

Since silicon oxynitride can interfere, the X-ray diffraction method described in EN 12698-2 may be used as an alternative.

9 Determination of free silica

9.1 Principle

This method is used to determine silica in silicon carbide, silicon nitride and other silica containing materials with a silica content greater than 0,03 %.

Determination of silica by reaction with hydrofluoric acid, distillation as H_2SiF_6 and subsequent determination of silicon via ICP-OES. This method is not influenced by other silicon compounds, so it is possible to analyse the silica content of materials such as silicon carbide and pure silicon.

9.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and of known analytical purity.

9.2.1 Distilled water, or water which has been fully demineralized by ion exchange (deionized water)

Unless otherwise specified, solutions are aqueous.

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9.2.2 Sodium hydroxide solution, c(NaOH) = 1 mol/l.

9.2.3 Hydrofluoric acid, ρ = 1,13 g/ml, c(HF) 40 % by mass.

9.2.4 Boric acid, H_3BO_3.

9.2.5 Silicon standard solution, (1,000 g $\pm$ 0,002) g Si/1 000 ml.

9.3 Apparatus

Normal laboratory apparatus and the following.

9.3.1 Analytical balance, capable of measuring to the nearest 0,05 mg.

9.3.2 Reaction vessel, such as a glassy carbon crucible with cover, or PTFE/PFA vessel with a screw cap. The cover or screw cap shall have a gas outlet in the centre and a small hole located off-centre (see Figure 3).

9.3.3 Absorption flask, polyethylene, 100 ml volumetric flask.

9.3.4 Aluminium heating-block, with temperature control from 50 °C to 150 °C.

9.3.5 Silicon-tubes.

9.3.6 PTFE-tubes and PTFE-stopper.

9.3.7 Electric suction-pump.

9.3.8 ICP-OES-spectrometer.

9.4 Sample preparation

Dry the test sample (sampled as described in clause 5) to constant mass at (110 ± 10) °C for a minimum of 2 h prior to analysis.

9.5 Procedure

Condition the absorption flask overnight by filling the flasks with diluted HF solution (approximately 2 % by mass). Dry the sample material for 1 h at (130 ± 10) °C. Depending on the expected SiO_2 concentration, weigh from 20 mg to 2 g, to the nearest 0,1 mg into a glassy-carbon crucible (or PTFE-vessel). Fill the absorption vessel with 50 ml NaOH solution (1 mol/l) and arrange the apparatus as shown in Figure 3.

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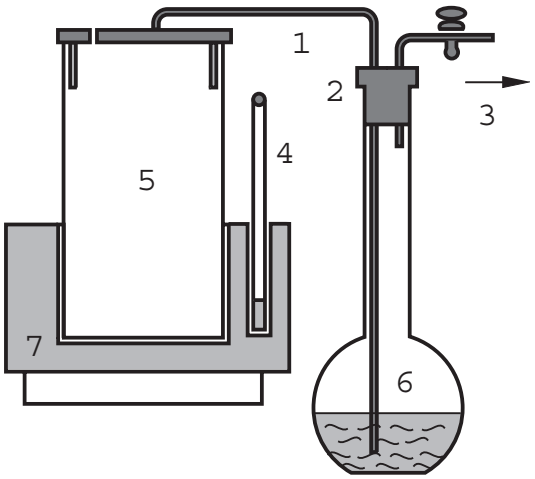

Key

1. PTFE tube
2. PTFE stopper
3. To suction pump
4. Thermocouple
5. Glassy carbon crucible with cover
6. Polyethylene volumetric flask
7. Aluminium heating block with temperature control

Figure 3 — Apparatus for determination of free silica

Switch on the pump to provide an air stream in the polyethylene flask producing about 10 bubbles/s. Take care that the glassy carbon cover closes tightly and control the tightness of the whole system.

NOTE A stream of air is allowed to enter the crucible through the small hole in the cover of the glassy carbon crucible (or the screw cap of the PTFE/PFA vessel).

Adjust the temperature to 50 °C and pipette 2 ml of hydrofluoric acid (HF 40 % m/m) onto the sample through the hole in the cover of the glassy carbon crucible (or the screw cap of the PTFE or PFA vessel).

Raise the temperature to 100 °C within 15 min and maintain that temperature for 45 min. The surplus HF is distilled. To ensure the reaction is complete, heat the crucible to 150 °C and switch off the heater 5 min after that temperature is attained. Allow the crucible to cool to ambient temperature, remove the cover and rinse the PTFE tube through the hole with distilled water. Switch off the pump and remove the PTFE tube from the polyethylene tube by rinsing.

Finally, add 1 g of H_3BO_3 to the absorption solution, dilute to volume with water and mix it thoroughly.

For the silicon measurement prepare a blank solution by adding 50 ml NaOH (1 mol/l), 2 ml HF (40 % m/m), and 1 g H_3BO_3 into a 100 ml polyethylene volumetric flask, dilute to volume with water and mix thoroughly.

Also prepare a standard solution by adding 50 ml NaOH (1 mol/l), 2 ml HF (40 % m/m) and 1 g H_3BO_3 into a 100 ml polyethylene volumetric flask. Depending on the expected silicon content of the sample, pipette silicon standard solution (see 9.2.5) into the prepared solutions. Dilute to volume with water and mix thoroughly.

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9.6 Determination

Determine the silicon concentration of the measuring solution using ICP-OES following the manufacturer's instructions.

9.7 Calculation and expression of SiO_2 content

Calculate the SiO_2 content, M_{SiO2}, as a percentage by mass using equation (6):

$$M_{SiO_2} = \frac{C_{Si} \times V \times f}{m} \times 100 \quad (6)$$

where

C_{Si} is the silicon concentration in the measuring solution, in mg/l;
V is the volume of the absorption flask, in ml;
m is the mass of the sample, in mg;
f is the factor SiO_2/Si, i.e. 2,139.

Express the result to the nearest 0,01 %.

9.8 Precision

Under the specified conditions, the values of the repeatability limit r, and the reproducibility limit R, as defined in ISO 5725-1 are:

r = 0,02 %;

R = 0,05 %.

NOTE 1 The results are based on silicon carbide and a mass fraction of 0,5 % SiO_2 mass fraction.

NOTE 2 R is an estimated value based on different inter-laboratory tests carried out by different working groups (GDMB-AK-Sonderwerkstoffe, DIN-NMP264).

10 Determination of carbon

NOTE Total carbon and free carbon are determined to calculate the chemically bound carbon.

10.1 Determination of the total carbon, C_t

Determine the total carbon in accordance with the procedures given in prEN ISO 21068.

10.2 Determination of free carbon, C_{free}

10.2.1 Hot chromic sulfuric iodic acid method

10.2.1.1 Principle

The method describes the decomposition of free carbon in silicon carbide by wet chemical oxidation.

This method does not imply the procedure is for detecting the released carbon dioxide. This method is applicable to free carbon contents of 0,01 % m/m to 5 % m/m. At higher concentrations incomplete recovery is possible.

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This method is applicable preferably to very fine grain powders (grain size less than 10 μm) or low contents of free carbon (less than 0,2 % m/m), as well as if there are evaporable and/or easily oxidizable components in the analysed silicon carbon.

The method releases organic carbon and carbonate carbon (as CO_2).

This free carbon of the sample is oxidized to carbon dioxide by chromic sulfuric iodic acid at 130 °C to 140 °C. The inert gas carries the CO_2 to a detection system of choice. Silicon carbide does not react under these conditions, or only to a negligible amount in case of very fine powders.

Unless otherwise specified, solutions are aqueous.

NOTE Coulometric, conductometric or infrared absorption CO_2 detection systems can be used. For determination of the released carbon dioxide, see Annex A.

10.2.1.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and of known analytical purity.

10.2.1.2.1 Distilled water, or water which has been fully demineralized by ion exchange (deionized water).

10.2.1.2.2 Drying agent, e.g. phosphorus pentoxide, P_2O_5.

10.2.1.2.3 Sodium dichromate, $Na_2Cr_2O_7.2H_2O$.

10.2.1.2.4 Potassium iodate, KIO_3.

10.2.1.2.5 Calcium carbonate, $CaCO_3$.

10.2.1.2.6 Sulfuric acid H_2SO_4, ρ = 1,84 g/ml.

10.2.1.2.7 Argon Ar, or **nitrogen N_2**, 99,998 % pure.

10.2.1.2.8 Chromic sulfuric iodic acid solution, prepared by dissolving 22 g of sodium dichromate (see 10.2.1.2.3) in 300 ml H_2O, and adding 700 ml sulfuric acid (see 10.2.1.2.6). The solution is heated for 30 min at (150 ± 10) °C, then 10 g of potassium iodate is added (see 10.2.1.2.4). After cooling, the solution is stored in a glass bottle.

WARNING — Chromic sulfuric iodic acid should be handled with care in accordance with local safety regulations.

10.2.1.3 Apparatus

Ordinary laboratory apparatus and the following:

10.2.1.3.1 Drying cupboard, with heating and temperature control up to (110 ± 5) °C.

10.2.1.3.2 Suitable crushing device, e.g. hard material mortar or mill with hard metal milling tools.

10.2.1.3.3 Analytical balance, capable of measuring to the nearest 0,05 mg.

10.2.1.3.4 Aluminium heating-block, with temperature control to (140 ± 5) °C.

10.2.1.3.5 Aluminium capsules, e.g. diameter 6 mm, length 15 mm, prepared from aluminium foil.

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10.2.1.3.6 Analytical sieve, mesh size 32 μm conforming to the requirements of ISO 3310-1.

10.2.1.3.7 Reaction vessel, with cooling device and drying trap (see Figure 4).

10.2.1.4 Sample preparation

For the wet chemical oxidation of sintered material, grain sizes of less than 32 μm are required. Materials of high carbon content shall not be used. Crush a piece of the sintered body in the crushing device (see 10.2.1.3.2). Sieve the crushed sample through the analytical sieve (see 10.2.1.3.6). Dry the test sample (sampled as described in clause 5) to constant mass at (110 ± 10) °C for a minimum of 2 h prior to analysis.

10.2.1.5 Procedure

Insert the reaction vessel into the heating block (see 10.2.1.3.4) and connect it via a cooler and drying trap with the chosen detection system. Adjust the carrier gas flow as required by the detection system used. Units with a sucking pump usually work with a surplus of carrier gas and pressure compensation. Optimize the gas flow so that no air is sucked into the system.

Adjust the temperature of the heating block to (130 ± 5) °C.

Pipette 30 ml of chromic sulfuric iodic acid (see 10.2.1.2.8) into the reaction vessel. To control the system, run a blank of 5 min to 10 min after a heating time of 20 min. Weigh, depending on the sample material and the expected content of free carbon, 20 mg to 200 mg of the dried sample (130 ± 5) °C to the nearest 0,1 mg into an aluminium capsule. Close the capsule with tweezers. Put the capsule in the sample insertion device in the reaction vessel and drop it into the hot chromic sulfuric iodic acid. At the same time the sample drops into the acid, switch on the measuring mode of the detection unit.

The total reaction time is 30 min. The detection time depends on the chosen detection system.

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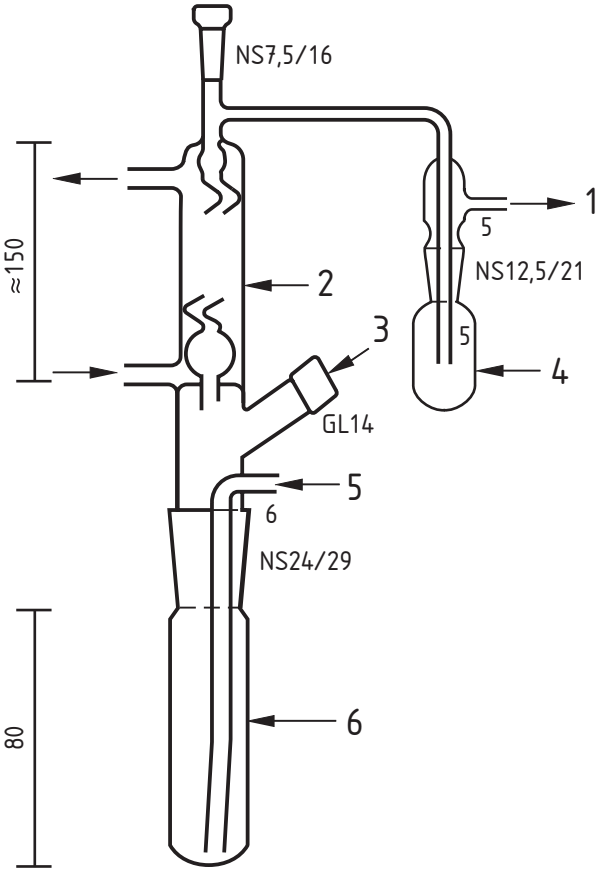
Dimensions in millimetres



Key

1. To detection unit
2. Cooler
3. Sample insertion device
4. Drying trap
5. Carrier gas inlet
6. Reaction vessel

Figure 4 — Example of a reaction vessel

10.2.1.6 Calculation and expression of results

Calculate the result graphically (see A.1) or, if using a state of the art coulometric device, by entering the sample mass into t he software and reading the result.

The graphically result expressed in impulses is changed to mass C_{free} by a coulometric factor and calculated as % by mass using the sample mass.

Express the result to the nearest 0,01 %.

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10.2.1.7 Precision

Under the specified conditions, the values of the repeatability limit r, and the reproducibility limit R, as described in ISO 5725-1 are:

r = 0,01 %;

R = 0,03 %.

NOTE 1 The results are based on silicon carbide and a content of 0,05 % to 0,5 % by mass C_{free}.

NOTE 2 R is an estimated value based on different inter-laboratory tests carried out by different working groups (GDMB-AK-Sonderwerkstoffe, DIN-NMP264).

11 Calculation of silicon carbide content

Calculate the silicon carbide content from the results of total carbon C_t and free carbon C_{free} determined in accordance with 10.1 and 10.2.

Calculate the silicon carbide content using equation (7):

$$SiC = (C_t - C_{free}) \times 3{,}3386 \quad (7)$$

where

C_t is the total carbon content determined in accordance with prEN ISO 21068;
C_{free} is the free carbon content determined in accordance with 10.2.

12 Determination of free alumina (Al_2O_3)

12.1 Principle

The unbound (free) alumina is dissolved out using a mixture of acids and determined in solution either by AAS or ICP.

12.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and of known analytical purity.

12.2.1 Distilled water, or water which has been fully demineralized by ion exchange (deionized water).

12.2.2 Sulfuric acid solution, 96 % (m/m).

12.2.3 Hydrofluoric acid solution, 40 % (m/m).

12.2.4 Nitric acid solution, 65 % (m/m).

12.2.5 Hydrochloric acid solution, 37 % (m/m).

12.2.6 Hydrochloric acid solution, approximately 4 % (m/m).

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12.3 Apparatus

Ordinary laboratory apparatus and the following:

12.3.1 Crucible, of PTFE (polytetrafluoroethylene) or platinum.

12.3.2 Sand bath.

12.3.3 Porcelain filter crucible, porosity 7 μm.

12.3.4 Volumetric flask, 250 ml.

12.3.5 Balance, capable of reading to the nearest 1mg.

12.4 Procedure

From the sample prepared as described in clause 5, take 5 g of test sample (m_0) weighed to the nearest 0,001 g and place it in the PTFE or platinum crucible. Add 20 drops of sulfuric acid (96 % m/m), 30 ml hydrofluoric acid (40 % m/m) and 10 ml nitric acid (65 % m/m) and leave the sample on a sand bath until evaporation is complete. Mix the residue with 10 ml hydrochloric acid (37 % m/m) and heat at approximately 60 °C for 30 min. Filter using a porcelain filter crucible. Wash the filtration residue three times with diluted hydrochloric acid (4 % m/m) and twice with hot distilled water (at approximately 90 °C to 100 °C), then dry in an oven at 110 °C. After cooling, determine the mass of the evaporated residue (m_1). Transfer the filtrate to a 250 ml volumetric flask. Cool, fill to the volume mark with distilled water and mix thoroughly.

Reserve the solution (V_0) to determine Al_2O_3.

12.5 Calculation and expression of results

After suitable dilution, determine the free aluminium oxide content by atomic absorption spectrometry (AAS) or inductively coupled plasma emission spectroscopy (ICP).

Calculate the free aluminium oxide content, Al_2O_{3free}, as a percentage by mass, using equation (8):

$$Al_2O_{3\,free} = A_{Al_2O_3} \times 5 \times d \qquad (8)$$

where

A_{Al2O3} is the concentration of Al_2O_3 in the solution reserved in 12.4 for determining Al2O3;
d is the dilution factor.

Report the result to the nearest 0,1 %.

12.6 Precision

There is currently no precision date available.

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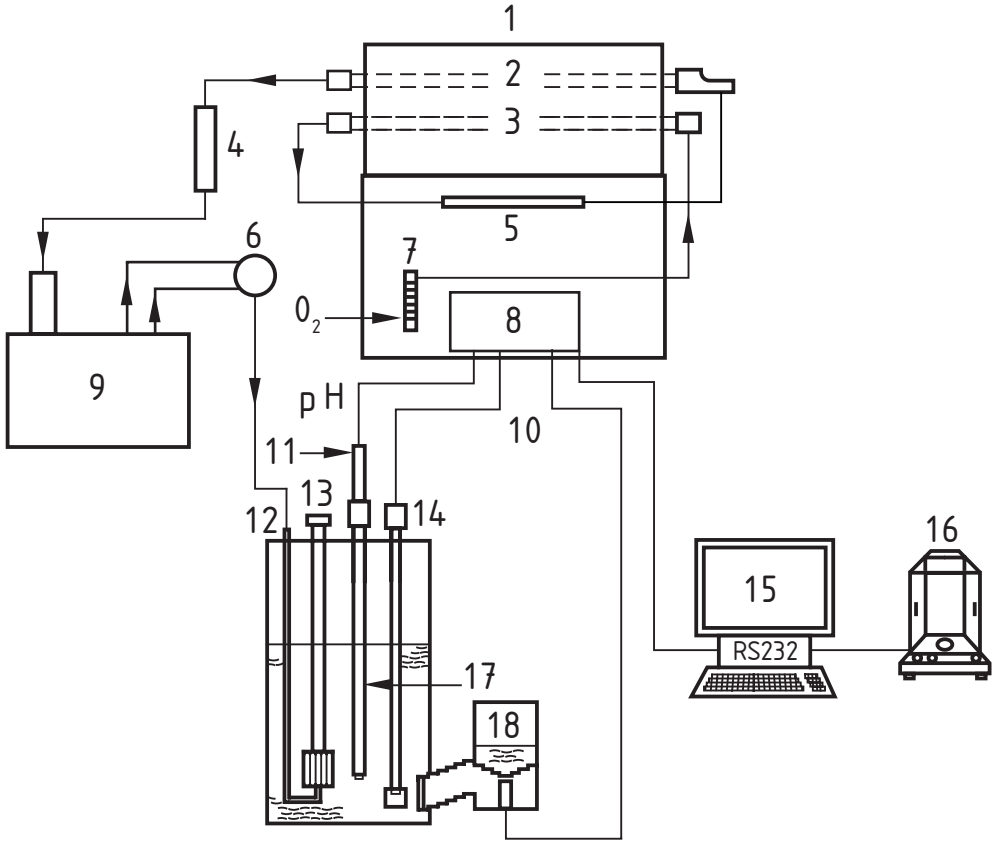
Annex A
(informative)

Determination of free carbon using the hot chromic sulfuric iodic acid method (10.2.1): Explanation for the evaluation of the different possible detection methods

A.1 Coulometric detection system

Coulometric detection systems record the total counts for a specific time interval (see Figure A.1). Therefore, it is not possible to draw running counts versus time or its first derivative.

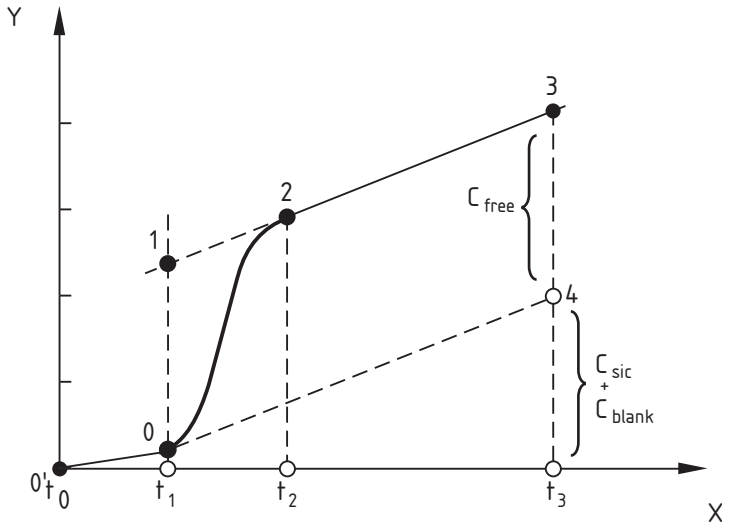
Using a suitable interface a measuring curve can be recorded by computer, the free carbon content can be evaluated (see Figure A.2).



Key

1. Furnace
2. Combustion tube
3. Oxygen purifying tube
4. SO_2 absorber
5. CO_2 absorber
6. 10% - 100% gas splitting valve
7. Flowmeter
8. Coulometer
9. Gas splitting pump
10. Electrolysis current
11. pH amplifier
12. Gas inlet tube
13. Basket stirrer
14. Cathode
15. PC
16. Balance
17. pH electrode
18. Anode

Figure A.1 — Coulometric detection system



Key

X = oxidation time	0' – 0 – 2 – 3	Oxidation curve	0 – 1	C_{free}
Y = CO_2 impulse	0' – 0	C_{blanc}	t_0	sample introduction
	0 – 2	$C_{free}+C_{SiC}+C_{blank}$	t_1	start of reaction C_{free}
	2 – 3	$C_{SiC}+ C_{blank}$	t_2	end of reaction C_{free}
			t_3	end of analysis

Figure A.2 — Example of the evaluation using a coulometric detection system

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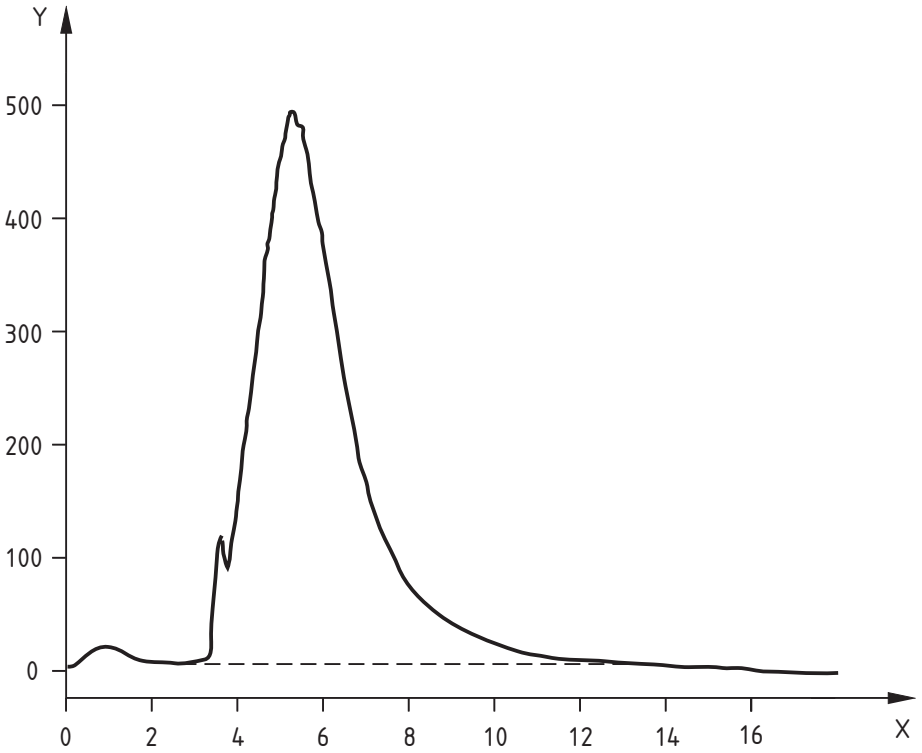
A.2 Infrared absorption detection system

For carbon dioxide detection via an infrared absorption system, the measuring signal can be recorded versus reaction time. The peak area is proportional to the amount of free carbon and is determined by electronic integration (see Figure A.3).



Key
X = time /min
Y = signal /mV

Figure A.3 — Example of the evaluation of CO_2-detection using an infrared absorption system

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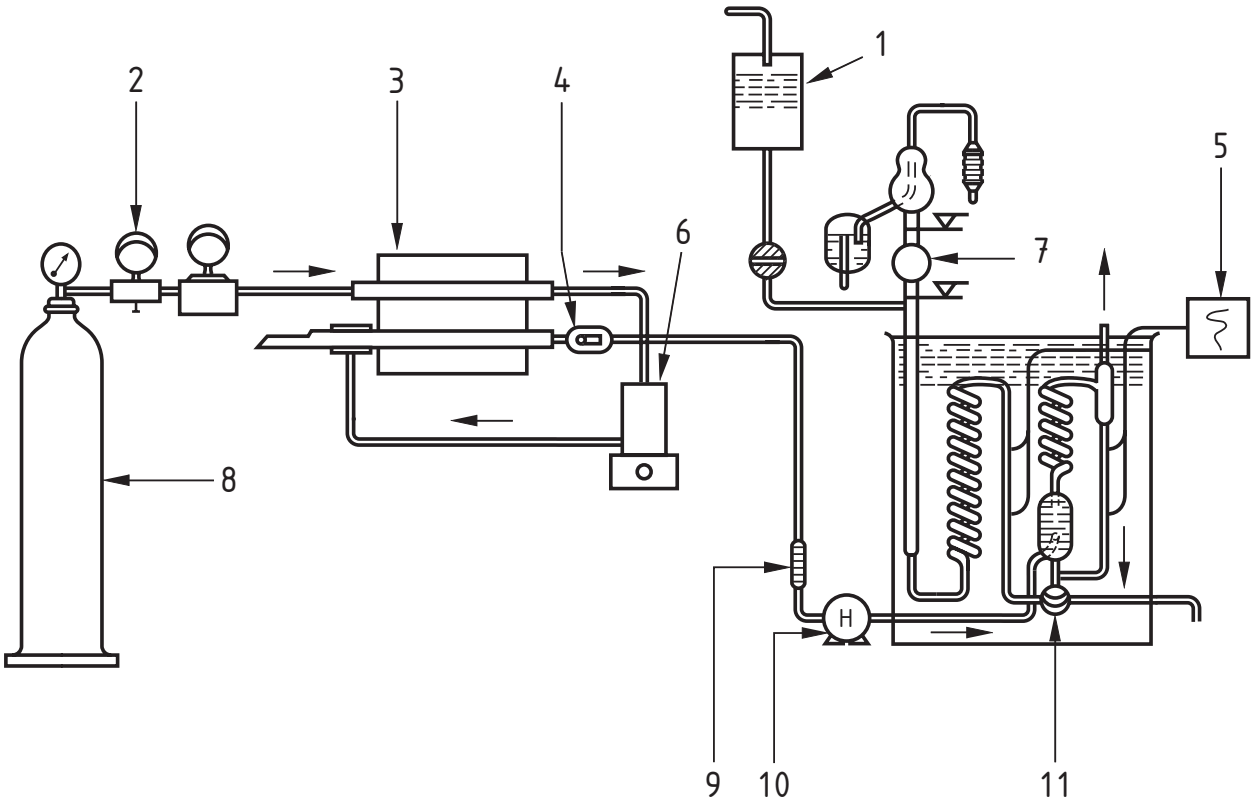
A.3 Conductometric detection system

The carbon dioxide from the reaction is absorbed into the sodium hydroxide solution after the sulfuric dioxide has been removed by percarbamide from the reaction gas. The absorbed carbon dioxide will proportionately reduce the amount of hydroxyl ions. This reduction is measured by the decrease of conductivity of the absorbing solution recorded versus the time by use of a self-compensating bridge connection (see Figure A.4).

If $d_k/dt = 0$, the measuring distance A (change in conductivity; Figure A.5) gives the amount of free carbon in proportion to previously determined calibrations.



Key

1. Stock container
2. Double pressure reducing valve
3. Furnace
4. Tube containing quartz wool
5. Self-balancing line recorder
6. Container filled with soda lime
7. Measuring vessel
8. Oxygen cylinder
9. Tube filled with percarbamide
10. Measuring pump
11. Conductivity measuring cell

Figure A.4 — Conductometric detection system

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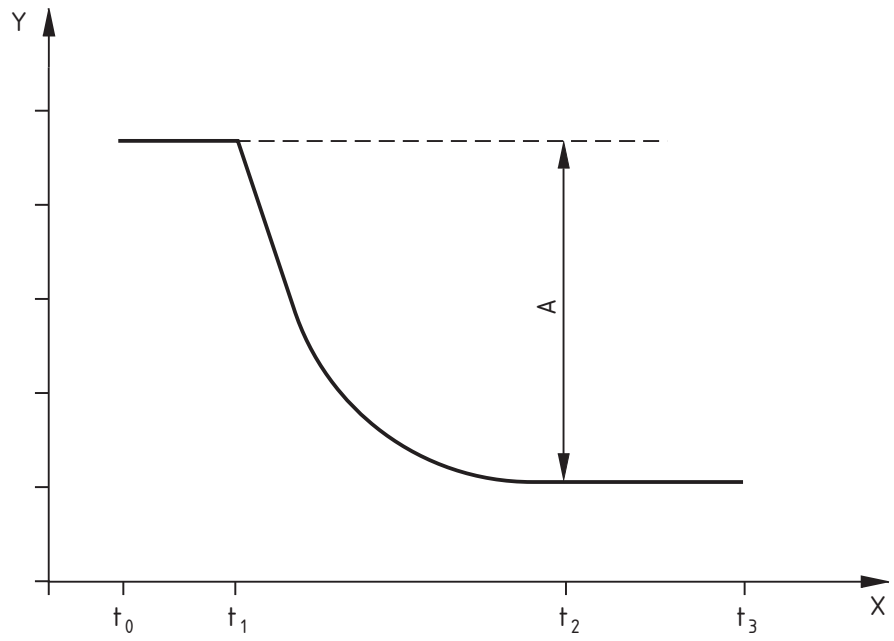

Key

X = time /min
Y = conductivity

t_0 Start of analysis
t_1 Start of reaction
t_2 End of reaction
t_3 End of analysis

Figure A.5 — Example of the evaluation using a conductometric system,

Bibliography

[1] EN 725-3 *Advanced technical ceramics — Methods of test for ceramic powders —Part 3: Determination of the oxygen content of non-oxides by thermal extraction with a carrier gas*

[2] EN 955-2 *Chemical analysis of refractory products — Part 2: Products containing silica and/or alumina (wet methods)*

[3] ENV 955-4 *Chemical analysis of refractory products — Part 4: Products containing silica and/or alumina (Analysis by Flame Atomic Absorption Spectrometry (FAAS) and Inductively Coupled Plasma Atomic Emission Spectrography (ICP)*

[4] EN ISO 12677 *Chemical analysis of refractory products by XRF — Fused cast bead method (ISO 12677:2003)*

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