



SLOVENSKI STANDARD

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Kemijska analiza nitrid silicijevega karbida - 1.del: Kemijske metode

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

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

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

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ICS 71.040.40

English Version

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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Contents

Page

Foreword	3
1 Scope	4
2 Normative references	4
3 Terms and Definitions	4
4 Methods for determination	4
5 Sampling	5
6 Determination of free aluminium	5
6.1 Principle	5
6.2 Reagents	6
6.3 Apparatus	6
6.4 Sample preparation	6
6.5 Procedure	6
6.6 Calculation and expression of results	6
7 Determination of total nitrogen	7
7.1 General	7
7.2 Determination of total nitrogen by carrier gas fusion (CGF)	7
7.3 Determination of total nitrogen content by fusion decomposition	10
7.4 Determination of total nitrogen content by Kjeldahl distillation	14
7.5 Determination of total nitrogen by microwave digestion	16
8 Determination of free silicon	18
9 Determination of free silica	18
9.1 Principle	18
9.2 Reagents	18
9.3 Apparatus	19
9.4 Sample preparation	19
9.5 Procedure	19
9.6 Determination	21
9.7 Calculation and expression of SiO ₂ content	21
9.8 Precision	21
10 Determination of carbon	21
10.1 Determination of the total carbon, C _t	21
10.2 Determination of free carbon, C _{free}	21
11 Calculation of silicon carbide content	25
12 Determination of free alumina (Al ₂ O ₃)	25
12.1 Principle	25
12.2 Reagents	25
12.3 Apparatus	26
12.4 Procedure	26
12.5 Calculation and expression of results	26
12.6 Precision	26
Annex A (informative) Determination of free carbon using the hot chromic sulfuric iodine acid method (10.2.1): Explanation for the evaluation of the different possible detection methods	27
A.1 Coulometric detection system	27
A.2 Infrared absorption detection system	29
A.3 Conductometric detection system	30
Bibliography	32

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.

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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 absorption onto soda lime, or by infrared detection.

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.

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 $(0,5 \pm 0,01)$ 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):

$$V_{(\text{STP})} = V_1 \times \frac{(p - p_{\text{H}_2\text{O}})}{1\,013,25} \times \frac{273}{(273 + T)} \quad (1)$$

where

V_1 is the measured volume, in ml;

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

$p_{\text{H}_2\text{O}}$ 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):

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

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.

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 %.

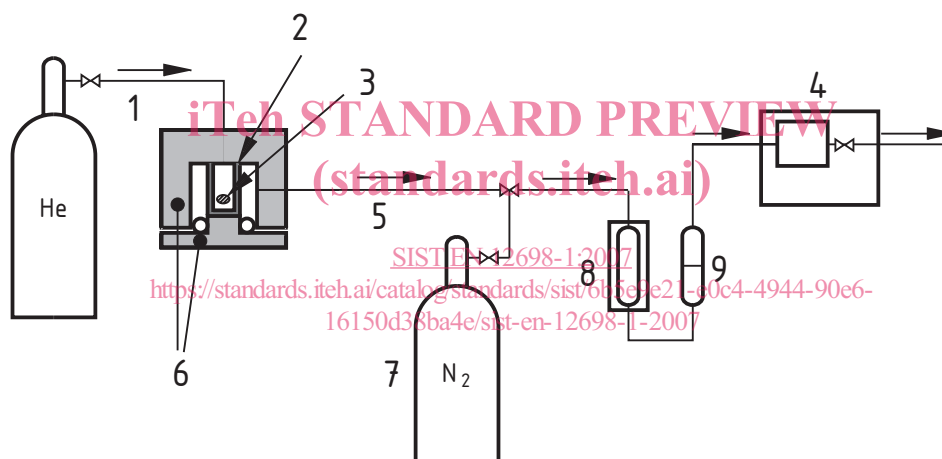
7.2.3.3 Nitrogen, having a minimum of 99,99 %.

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 | 5. He plus gases from sample | 8. Apparatus for oxidizing carbon monoxide and hydrogen (CO → CO ₂ ; H ₂ → H ₂ O) |
| 2. Crucible | 6. Electrodes | 9. Carbon dioxide and water vapour absorption tubes (H ₂ O↓ CO ₂ ↓) |
| 3. Sample | 7. Calibration gas | |
| 4. Thermal conductivity cell | | |

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.

7.2.5 Sample preparation

Dry the test sample to constant mass at $(110 \pm 10) ^\circ\text{C}$. 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 $100 ^\circ\text{C}$ 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

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7.2.7.1 Gas calibration (standards.iteh.ai)

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

$$m = \frac{p \times V_T \times \rho_{N_2}}{p_n (1 + \gamma \times T)} \quad (3)$$

where

p is the corrected barometric pressure, in hPa;

T is the temperature, in $^\circ\text{C}$;

V_T is the gas volume added, in ml at $T ^\circ\text{C}$ and p hPa;

ρ_{N_2} 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 ($0,003\ 671\ \text{K}^{-1}$);

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.

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:

$$r = 1 \%$$

$$R = 2 \%$$

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

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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, $\rho = 1,84$ g/ml.

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