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Kemijska analiza nitrid silicijevega karbida - 2.del: XRD metode

Chemical analysis of nitride bonded silicon carbide refractories - Part 2: XRD methods

Chemische Analyse von feuerfesten Erzeugnissen aus nitridgebundenem Silicumcarbid - Teil 2: XRD-Verfahren

Analyse chimique des produits réfractaires contenant du carbure de silicium a liaison nitrure - Partie 2 : Méthodes de DRX

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Chemical analysis of nitride bonded silicon carbide refractories - Part 2: XRD methods

Analyse chimique des produits réfractaires contenant du carbure de silicium à liaison nitrure - Partie 2 : Méthodes de DRX

Chemische Analyse von feuerfesten Erzeugnissen aus nitridgebundenem Silicumcarbid - Teil 2: XRD-Verfahren

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Foreword

This document (EN 12698-2:2007) 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of an identical text or by endorsement, at the latest by September 2007, and conflicting national standards shall be withdrawn at the latest by September 2007.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.

1 Scope

This standard describes methods for the determination of mineralogical phases typically apparent in nitride and oxy-nitride bonded silicon carbide refractory products using a Bragg-Brentano diffractometer.

It includes details of sample preparation and general principles for qualitative and quantitative analysis of mineralogical phase composition. Quantitative determination of α-Si_3N_4, β-Si_3N_4, Si_2ON_2, AlN, and SiAlON are described.

NOTE For the refinement procedures the total nitrogen content, analysed in accordance with EN 12698-1 is needed.

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 12698-1, *Chemical analysis of nitride bonded silicon carbide refractories — Part 1: Chemical methods*

ISO 836:2001, *Terminology for refractories*

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

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

3 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 a precursor material, which undergoes a phase transformation in an oxygen-free nitrogen atmosphere.

4 Apparatus

Bragg-Brentano diffractometers with a copper X-ray tube, graphite monochromator and scintillation counter and the following experimental setting for data collection are used:

— goniometer with a measurement uncertainty of ≤ 0,5 ° at a confidence level of 95 %;

— primary soller slit with a divergence ≤ 2,5 °;

— divergence slit 1 °;

— receiving slit ≤ 0,2 mm;

— scatter slit ≤ 1 °;

— narrow line focus;

— tube settings 40 kV and 20 mA to 45 mA.

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 Procedure

6.1 Sample preparation

Grind the sample using a mill so that the resultant powder can pass through a 100 mesh sieve.

NOTE Care should be taken not to grind the sample excessively as this has been found to cause the silicon nitride, and silicon phases in particular, to reduce in intensity. This is believed to be due to a build up of an amorphous layer on their particles due to damage induced by the silicon carbide.

Press the powder into the cavity holder from the reverse side of the cavity to that which is to be presented to the x-ray beam (to reduce preferred orientation). The depth of the cavity shall be sufficient to exceed the critical depth of CuKα radiation for the sample analysed.

6.2 Measuring parameters

Scan the sample on the instrument using the following parameters:

— start angle, 2θ 10 °;

— end angle, 2θ 70 °, 130 ° if β-SiAlON determination is required;

— step-spec, 2θ 0,02 ° or continuous;

— integration time 4 s.

An additional scan using the same conditions as above between 60 ° and 70 ° 2θ may be required if aluminium and/or iron is thought to be present.

NOTE Parameters for tube settings should be: voltage 40 kV, excitation current 20 mA to 45 mA.

6.3 Qualitative analysis

Use an automatic or manual search to identify different phases in accordance with the ICDD, JCPDS and ASTM databases.

NOTE 1 A deconvolution program should be used for overlapping peaks.

NOTE 2 The following phases are commonly found in nitride bonded silicon carbide:

α-SiC, β-SiC, α-Si3N4, β-Si3N4, Si (free), Si2ON2, SiO2 (cristobalite), FeSi2 and WC (from grinding). Less common phases include:

FeSi, Fe, Al, AlN, C (graphite), SiO2 (quartz), SiAlON.

Some potential line overlaps to be aware of include the (111) cristobalite at 28,4 ° with the (111) silicon and the (110) iron at 44,7 ° with the (200) aluminium, there is also an interference of monoclinic zirconia on silicon.

6.4 Quantitative analysis

6.4.1 General

For quantitative analysis the net peak intensities of the test sample are compared to a sample of known concentration. The intensities shall be evaluated by measuring the peak height or preferably the peak area. For the determination of the net peak intensity, deduct the background from the total peak intensity.

Certified reference material(s) should be used where available.

If no reference material is available chemical and mineralogical pure substances may be used instead.

Calibration mixtures of 5 % and 10 % by mass in silicon carbide matrix shall be made up. Calibrations using the above mixes and one of 100 % by mass of silicon carbide by mass shall be constructed.

The phases given in Table 1 can currently be quantified by XRD. For quantification, the peak positions listed in Table 1 shall be preferably used. Ascertain that there are no line overlaps with other phases by performing a qualitative analysis in accordance with 6.3.

Table 1 — Phases which can currently be quantified by XRD

Phase	Available reference material	Diffraction angle *2θ* degrees	Miller Indices
α-Si_3N_4	NIST656 BAM-S001	20,5 ° 31,0 °	101 201
β-Si_3N_4	NIST656	27,0°	200
Si		28,4 ° 47,3 ° 56,0 °	111 220 311
Si_2ON_2		19,0 ° 20,0 °	110 020
SiO_2 (cristobalite)	NBS SRM 1879	21,9 °	101
$FeSi_2$	BCS 305/1 (50 % $FeSi_2$, 50 % Si)	17,1 °	001
FeSi		28,0 ° 69,4 ° 79,9 °	110 311 321
Fe		44,7 ° 82,3 °	110 211
Al		44,7 ° 78,2 ° 82,4 °	200 311 222
α-SiC			Used for calibration material

NOTE 1 The limits of determination can be ≥ 5 % by mass even when using the recommended apparatus in clause 4 and measuring parameters in 6.2.

NOTE 2 Peak intensities should be measured as areas using computer software, taking into account peak overlaps where appropriate. Measuring the peak height and the background by hand is also possible.

NOTE 3 It can be appropriate to use mass absorption coefficients based on bulk chemistry in the calculation of components particularly when non silicon based components are present. If so, it should be noted in the test certificate.

6.4.2 Calculation

6.4.2.1 General

The net intensities are assumed to correlate linearly with the phase concentration. Therefore, the determination of the unknown phase concentration shall be calculated by the rule of proportion.

Where more than one peak per phase is measured, a mean result shall be quoted. The amount of each phase shall be taken from its individual calibration.

6.4.2.2 Calculation refinement for α-Si_3N_4, β-Si_3N_4, Si_2ON_2, and AlN

The contents of α-Si_3N_4, β-Si_3N_4, Si_2ON_2, and AlN shall be normalized in proportion to their molecular nitrogen contents to the total nitrogen concentration. Determine the total nitrogen content in accordance with EN 12698-1.

EXAMPLE

By XRD, the following results were obtained.

α-Si_3N_4 1,0 % by mass;

β-Si_3N_4 2,0 % by mass;

Si_2ON_2 3,0 % by mass.

The total nitrogen was determined to be 2,10 % by mass from chemical methods (see EN 12698-1).

Calculating the nitrogen content from the XRD results gives:

nitrogen from α-Si_3N_4 = $\frac{1{,}00 \times 56{,}03}{140{,}29} = 0{,}40$ % by mass;

nitrogen from β-Si_3N_4 = $\frac{2{,}00 \times 56{,}03}{140{,}29} = 0{,}80$ % by mass;

nitrogen from Si_2ON_2 = $\frac{3{,}00 \times 28{,}02}{100{,}19} = 0{,}84$ % by mass.

Therefore the total nitrogen from XRD data = 2,04 % by mass;

and therefore the correction factor is: $\frac{2{,}10}{2{,}04}$

which gives the true nitride content as:

α-Si_3N_4 1,0 % by mass;

β-Si_3N_4 2,1 % by mass;

Si_2ON_2 3,1 % by mass.