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Chemical analysis of raw materials and refractory products containing silicon-carbide, silicon-nitride, silicon-oxynitride and sialon —

Part 4:
XRD methods

Analyse chimique des matières premières et des produits réfractaires contenant du carbure de silicium, du nitrure de silicium, de l'oxynitrure de silicium et du SiAlON —

Partie 4: Méthodes de DRX

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Contents

Foreword

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A list of all parts in the ISO 21068 series can be found on the ISO website.

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Introduction

The ISO 21068 series has been developed from the combination of EN 12698-1:2007[1] and EN 12698-2:2007[2] and ISO 21068-1:2008,[3] ISO 21068-2:2008[4] and ISO 21068-3:2008.[5] The last three standards have been originally developed from the combination of Japanese standard JIS R 2011:2007[6] and work items developed within CEN. Because there is a wide variety of laboratory equipment in use, the most commonly used methods are described.

This document is derived from EN 12698-2:2007[2] describing XRD methods for the determination of mineralogical phases typically apparent in nitride and oxy-nitride bonded silicon carbide refractory products using a Bragg-Brentano diffractometer.

Chemical analysis of raw materials and refractory products containing silicon-carbide, silicon-nitride, silicon-oxynitride and sialon —

Part 4:
XRD methods

1 Scope

This document 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 preparations and general principles for qualitative and quantitative analyses of mineralogical phase composition. Quantitative determination of α-Si_3N_4, β-Si_3N_4, Si_2ON_2, AlN, and β’- SiAlON are described.

For quantitative determination of α-Si_3N_4, β-Si_3N_4, Si_2ON_2, AlN and β’-SiAlON refinement procedures based on the total nitrogen content of the sample are described.

NOTE ISO 21068-3 is used for the analysis of the total nitrogen content of the sample.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

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*

ISO 10081-4, *Classification of dense shaped refractory products — Part 4: Special products*

ISO 21068-1, *Chemical analysis of raw materials and refractory products containing silicon-carbide, silicon-nitride, silicon-oxynitride and sialon — Part 1: General information and sample preparation*

ISO 21068-3, *Chemical analysis of raw materials and refractory products containing silicon-carbide, silicon-nitride, silicon-oxynitride and sialon — Part 3: Determination of nitrogen, oxygen and metallic and oxidic constituents*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 21068-1 and ISO 10081-4 apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

4 Apparatus

The aim is to have a high resolution diffractogram with well-defined peaks on a low background with minimal artefacts due to fluorescence and Kβ peaks. A Bragg-Brentano diffractometer with a copper X-ray tube operating at 40 kV and 20 mA to 45 mA. Primary beam monochromation is achieved using a suitable filter or primary beam monochromator or equivalent. Secondary beam monochromation is achieved using a graphite monochromator, energy discriminator or equivalent. The following components and settings for data collection are used:

- goniometer with a measurement uncertainty of ≤0,5° at a confidence level of 95 %;
- suitable primary and secondary slit arrangements include variable slots or fixed slits with a primary soller slit with a divergence ≤2,5°;
- divergence slit 1°;
- receiving slit ≤0,2 mm;
- scatter slit ≤1°.

5 Sampling

Sample shaped and unshaped products in accordance with 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.

Follow the sampling and grinding procedure as described in ISO 21068-1.

6 Procedure

6.1 Sample preparation

Grind the sample using a mill so that the resultant powder can pass through a 150 µm sieve. The sample should not be ground excessively.

NOTE Grinding the sample excessively 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 uniformly into the cavity of the sample holder to ensure a flat surface that is exposed to the X-ray beam. If preferred orientation of the sample becomes an issue, this can be reduced using a back fill sample holder. 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-size, 2θ 0,02° or continuous;
- integration time 4 s.

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

Values for tube parameters 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. A deconvolution program should be used for overlapping peaks.

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

- α-SiC, β-SiC, α-Si_3N_4, β-Si_3N_4, Si (free), Si_2ON_2, SiO_2 (cristobalite), $FeSi_2$ and WC (from grinding);
- Less common phases include: FeSi, Fe, Al, AlN, C (graphite), SiO_2 (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 area. For the determination of the net peak intensity, deduct the background from the total peak intensity.

Primary standards or certified reference materials shall be used.

If no reference material is available, chemical and mineralogical pure substances can 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		20,5° 31,0°	101 201
β-Si_3N_4		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)	NIST 1879b	21,9°	101
$FeSi_2$		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 as calibration sample

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.

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 2 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 is 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 of their molecular nitrogen contents to the total nitrogen content of the sample. Determine the total nitrogen content of the sample in accordance with ISO 21068-3.

EXAMPLE

By XRD, the following results were obtained.

- α-Si_3N_4 1,0 mass percent;
- β-Si_3N_4 2,0 mass percent;
- Si_2ON_2 3,0 mass percent.

The total nitrogen was determined to be 2,10 mass percent from chemical methods (see ISO 21068-3).

Calculating the nitrogen content from the XRD results gives:

- nitrogen from α-Si_3N_4 = $\frac{1,00 \times 56,03}{140,29} = 0,40$ mass percent;
- nitrogen from β-Si_3N_4 = $\frac{2,00 \times 56,03}{140,29} = 0,80$ mass percent;
- nitrogen from Si_2ON_2 = $\frac{3,00 \times 28,02}{100,19} = 0,84$ mass percent.

Therefore, the total nitrogen from XRD data is 2,04 mass percent and therefore, the correction factor is:

$$\frac{2,10}{2,04} = 1,029$$

Which gives the true nitride contents of the sample as:

- α-Si_3N_4 1,0 mass percent;
- β-Si_3N_4 2,1 mass percent;
- Si_2ON_2 3,1 mass percent.

NOTE This method does not work if SiAlON or glassy phases of nitrides are present.

6.4.2.3 Calculation refinement for *β'*-SiAlON content

6.4.2.3.1 Determination of composition

As the composition of the β'-SiAlON is variable, it is necessary to first accurately determine the composition and then the amount of β'-SiAlON and other nitride or oxynitride components. The determination of composition or *z*-value is made by XRD, for the stoichiometric formula $Si_{(6-z)}Al_zO_zN_{(8-z)}$.

Accurately determine the peak positions of all non-overlapped β'-SiAlON peaks using an appropriate certified reference material or standard such as NBS SRM 640 silicon powder to check alignment.

Reference the β'-SiAlON diffraction peaks on the basis of *h, k, l* Miller indices for a hexagonal structure. Annex A lists the calculated positions for β'-SiAlON for $z = 3$, along with Miller indices and some potential overlap peaks.

Calculate the nitrogen content of the β'-SiAlON using the *z*-value to give the composition.

EXAMPLE 1

For $z = 1$, the resulting stoichiometric formula for the β'-SiAlON is Si_5AlON_7. The calculated nitrogen content of Si_5AlON_7 is 34,8 mass percent.

If no other nitride phases (α-Si_3N_4, β-Si_3N_4, AlN or $SiON_2$) are present, determine the total nitrogen content of the sample according to ISO 21068-3. Calculate the *β'*-SiAlON content of the sample from the total nitrogen content and the calculated nitrogen content of the SiAlON using Formula (1).

$$S_\beta = \frac{N}{N_\beta} \times 100 \tag{1}$$

where

S_β is the β'-SiAlON content, in mass percent;

N is the total nitrogen content of the sample, in mass percent;

N_β is the calculated nitrogen content of β'-SiAlON, in mass percent;

EXAMPLE 2

Total nitrogen content of the sample: N = 6,0 %;

z-value = 1, resulting in a calculated nitrogen content of β'-SiAlON of N_β = 34,8 %;

The β'-SiAlON content of the sample is then calculated using Formula (1):

$$S_\beta = \frac{6{,}0}{34{,}8} \times 100 = 17{,}2\ \%$$

If other nitride phases are present, use XRD as described in 6.4.1 and 6.4.2.2. Assign any residual nitrogen to SiAlON and determine the β'-SiAlON content.

NOTE It is possible that normalizing to the total oxygen content might not take into account the presence of silicate glass.

Details of the X-ray diffraction data are given in Annex A.

6.4.2.3.2 Determination of *z*-value

Determine the cell parameters using appropriate methods; proprietary software or other techniques may be used.

NOTE Cohen's least-squares method (see 6.4.2.3.3) is a suitable technique for a hexagonal SiAlON.

Calculate the a_0 and c_0 values using Formulae (4) to (11). From the a_0 and c_0 values, use the curves from Reference [7] to determine the z-value using Formulae (2) and (3):

$$z = \frac{(a_0 - 7{,}605)}{0{,}027\,8} \qquad (2)$$

$$z = \frac{(c_0 - 2{,}91)}{0{,}024\,8} \qquad (3)$$

If the values of z differ, take the arithmetic mean. Apply the z-value to the SiAlON formula:

$$\mathrm{Si}_{(6-z)}\mathrm{Al}_z\mathrm{O}_z\mathrm{N}_{(8-z)}$$

An example for the determination of the z-value is given in Annex A.

6.4.2.3.3 Cohen’s least squares method (Reference [8])

For each β’-SiAlON peak (in °2θ) calculate the following parameters:

$\sin^2\theta$ (rads), $\cos^2\theta$ (rads)

and from the reflection indices

$$\alpha = h^2 + hk + k^2 \qquad (4)$$

$$\gamma = l^2 \qquad (5)$$

$$\delta = 10\sin^2(2\theta)\times\left(\frac{1}{\sin\theta}+\frac{1}{\theta}\right)1 \qquad (6)$$

For each diffraction peak, calculate values of α^2, $\alpha\gamma$, $\alpha\delta$, γ^2, $\gamma\delta$, δ^2, $\gamma\sin^2\theta$, $\delta\sin^2\theta$ and sum the individual factors over all the reflections.

Set up and solve three simultaneous formulae:

$$\sum\alpha^2 A_0 + \sum\alpha\gamma C_0 + \sum\alpha\delta D = \sum\alpha\sin^2\theta \qquad (7)$$

$$\sum\alpha^2 A_0 + \sum\gamma^2 C_0 + \sum\gamma\delta D = \sum\gamma\sin^2\theta \qquad (8)$$

$$\sum\alpha\delta A_0 + \sum\gamma\delta C_0 + \sum\delta^2 D = \sum\delta\sin^2\theta \qquad (9)$$

Solve for A_0, C_0 and D and then

$$a_0 = \sqrt{\lambda^2/3A_0} \qquad (10)$$

$$c_0 = \sqrt{\lambda^2/4C_0} \qquad (11)$$

where λ is the wavelength of radiation, in Ångström.

7 Precision

7.1 Repeatability

The absolute difference between two independent single test results obtained under repeatability conditions will not be greater than 1 % in more than 5 % of cases.

7.2 Reproducibility

Reproducibility data is currently not available.

8 Test report

The test report shall be presented in accordance with ISO 21068-1.

Annex A
(informative)

X-ray diffraction data for the determination of β'-SiAlON content

A.1 General

The data given in Table A.1 is derived from References [7] and [8].

Table A.1 — Theoretical peak positions and Miller indices (*h, k, l*) of *β*'-SiAlON for *z* = 3

d-spacing (Å)	2*θ* (°) CuKα	*h*	*k*	*l*	Potential overlapping peaks
6,650	13,302	1	0	0	
3,840	23,145	1	1	0	
3,325	26,787	2	0	0	
2,715	32,962	1	0	1	
2,514	35,688	2	1	0	α-SiC, β-SiC
2,351	38,245	1	1	1	α-SiC
2,217	40,664	3	0	0	
1,920	47,307	2	1	1	Si metal
1,845	49,365	3	1	0	
1,777	51,361	3	0	1	
1,613	57,049	2	2	1	
1,568	58,862	3	1	1	
1,526	60,642	3	2	0	
1,487	62,391	0	0	2	α-Si_3N_4
1,451	64,112	4	1	0	
1,387	67,483	1	1	2	
1,358	69,137	3	2	1	
1,330	70,774	5	0	0	α-SiC
1,304	72,394	4	1	1	
1,280	74,000	3	3	0	
1,257	75,593	4	2	0	α-SiC, β-SiC, β-Si_3N_4
1,235	77,174	3	0	2	
1,214	78,746	5	0	1	
1,194	80,309	5	1	0	α-Al_2O_3, α-Si_3N_4
1,176	81,865	2	2	2	α-Si_3N_4
1,158	83,415	4	2	1	α-Si_3N_4, β-Si_3N_4
1,108	88,041	5	1	1	
1,093	89,578	4	3	0	
1,065	92,653	3	2	2	
1,039	95,736	4	1	2	
1,026	97,283	4	3	1	
1,014	98,836	6	1	0	
1,003	100,395	5	2	1	