Advanced technical ceramics — Methods of test for ceramic powders —

Part 4: Determination of oxygen content in aluminium nitride by XRF analysis

The European Standard EN 725-4:2006 has the status of a British Standard

ICS 81.060.30

British Standards

National foreword

This British Standard was published by BSI. It is the UK implementation of EN 725-4:2006. It supersedes DD ENV 725-4:1994 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee RPI/13, Advanced technical ceramics.

A list of organizations represented on RPI/13 can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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English Version

Advanced technical ceramics - Methods of test for ceramic powders - Part 4: Determination of oxygen content in aluminium nitride by XRF analysis

Céramiques techniques avancées - Méthodes d'essai pour poudres céramiques - Partie 4: Détermination de la teneur en oxygène du nitrure d'aluminium par spectrométrie de fluorescence XRF

Hochleistungskeramik - Prüfverfahren für keramische Pulver - Teil 4: Bestimmung der Sauerstoffgehaltes in Aluminiumnitrid-Pulvern mittels Röntgenfluoreszensanalyse (RFA)

This European Standard was approved by CEN on 13 March 2006.

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Foreword

This European Standard (EN 725-4:2006) has been prepared by Technical Committee CEN/TC 184 “Advanced technical ceramics”, 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of an identical text or by endorsement, at the latest by October 2006, and conflicting national standards shall be withdrawn at the latest by October 2006.

This European Standard supersedes ENV 725-4:1994.

The main changes in the new edition are:

- revision of the foreword to reflect changes in the EN 725 series;

- changes to the normative references;

- modification of the test piece preparation requirements;

- modification of the test report requirements;

- addition of a bibliographical reference.

EN 725 *Advanced technical ceramics — Methods of test for ceramic powders* was prepared in Parts as follows:

Part 1: *Determination of impurities in alumina*

Part 2: *Determination of impurities in barium titanate*

Part 3: *Determination of oxygen content of non-oxides by thermal extraction with a carrier gas*

Part 4: *Determination of oxygen content in aluminium nitride by XRF analysis*

Part 5: *Determination of particle size distribution*

Part 6: *Determination of specific surface area* [withdrawn]

Part 7: *Determination of absolute density* [withdrawn]

Part 8: *Determination of tapped bulk density*

Part 9: *Determination of un-tapped bulk density*

Part 10: *Determination of compaction properties*

Part 11: *Determination of densification on natural sintering*

Part 12: *Chemical analysis of zirconia*

Parts 6 and 7 of the series were superseded in 2005 by EN ISO 18757 and EN ISO 18753 respectively.

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1 Scope

This European Standard specifies a method for the determination of oxygen contents of 2 % or less in aluminium nitride powder, by XRF analysis.

2 Normative references

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

EN 725-5, *Advanced technical ceramics — Methods of test for ceramic powders — Part 5: Determination of particle size distribution*

EN ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:2005)*

EN ISO 18757, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of specific surface area of ceramic powders by gas adsorption using the BET method (ISO 18757:2003)*

3 Principle

The sample is compacted to obtain a pellet, and the net intensity of the oxygen K_α characteristic (I_0 K_α) of the pellet is measured by XRF spectrometer. The net intensity is the background intensity subtracted from the peak intensity at the peak position. The oxygen content in the sample is determined from this net intensity and by reference to previously defined calibration graphs; the calibration graph expresses the direct relation between net intensity and oxygen concentration. Calibration standards are prepared from different mixtures of fine aluminium nitride powder and a fine alumina powder.

4 Apparatus and experimental conditions

4.1 Apparatus

Sequential X-ray fluorescence spectrometer, equipped with a multilayer pseudo crystal and a gas flow proportional counter.

NOTE For further details, see EN ISO 12677.

4.2 Experimental conditions

The experimental conditions depend on the apparatus, with an example of good practice being as follows:

a) Mode: vacuum

b) Excitation: tube voltage: 30 kV
tube current: 95 mA

c) Spectrometer: crystal: multilayer pseudo crystal
2 d = 55 Å

d) Peak: wavelength: 23,62 Å
energy: 0,525 keV
angular position: 51° 2θ (to be adjusted)

e) Detection: detector type: gas flow proportional counter $Ar\text{-}CH_4$ or $He\text{-}CO_2$
pulse height selection: the discriminate levels (V_{min}, V_{max}) should be set so as:
$V_{min}, V_{max} = V \pm 1{,}3\ W$
where W is the width at half height of the pulse amplitude distribution peaking at V (this allows more than 99,7 % of the pulse amplitude distribution to pass through the window)

f) Background: Background intensity at the peak position is obtained using a linear regression between two background measurements before and after the fluorescence peak wavelength: 23,62 Å
The recommended positions (2θ min, 2θ max) are:

$$2\theta \text{ min, max} = 2\theta_\rho \pm 4\ W_\rho$$

where $2\theta_\rho$ is the peak position
W_ρ is the peak width at half height of the peak

g) Counting time: 100 s for both peak and background measurements; total counting time 300 s

5 Sample preparation

5.1 Granulometry

Powders shall be fine enough to obtain a good homogeneous pellet without a binder. The particle size distribution, determined in accordance with EN 725-5, shall be between 10 µm and 2 µm with an equivalent diameter corresponding to 50 % of the grain size.

NOTE Grinding the sample may increase the oxygen content of the powder.

5.2 Test piece preparation

5.2.1 Where comparatively large (10 g) samples are available, pour the powder into a die (e.g. 40 mm in diameter) and compact it. The powder may be placed in an aluminium cup before pressing if required.

5.2.2 For smaller samples (2 g), press the powder on to a backing plate made of cellulose or boric acid powder. The aluminium cup may again be used if required.

5.2.3 Prepare two samples for each determination.

NOTE In most quantitative analysis, sample thickness is considered as infinite. If critical thickness is the thickness that would yield 99,9 % of the maximum intensity, calculation shows that critical thickness increased from 2,9 µm to 3,35 µm when oxygen concentration in AlN increases from 0,5 % to 10 %.

6 Calibration

6.1 Preparation of standards

Prepare calibration standards from mixtures of aluminium nitride powder in accordance with 5.1 and alumina powder with a specific surface area of about 6 m^2/g according to EN ISO 18757 and an equivalent diameter corresponding to 50 % of the distribution, normally 1 µm or less. Mix the powders for at least 10 min in an agate mortar and pestle, and vibrate the mixture for 1 min.

6.2 Calibration curves

Establish curves which record the oxygen (K_α) net intensity with the oxygen mass fraction in the different calibration mixtures.

As aluminium nitride powders used in calibration mixtures are not oxygen free, an addition method shall be used in order to determine the total oxygen concentration. In this method, a known amount of oxygen, $\Delta[O]$, is added to the sample. Fluorescence intensities I_1 and I_2, before and after addition, are used to extrapolate to the unknown concentration. If linearity is assumed:

$$\frac{[O]}{\Delta[O]} = \frac{I_1}{I_1 - I_2}$$

The addition method is limited to fairly low concentrations, usually less than 1 %. Thereby, the use of an aluminium nitride powder with oxygen concentration ≤ 1 % is recommended for calibration purposes.

The shape of the calibration curve depends on the oxygen concentration range, but within a range of 0 % to 5 %, a linear regression is likely to be convenient.

6.3 Recalibration

Recalibration is needed in order to check long term instrumental drift. An aluminium nitride sintered pellet with a flat polished surface can be used to shift the calibration curve. The oxygen content of this reference standard should not be lower than 3 % in order to obtain a good signal intensity level.

Another solution, which is more time consuming, consists in the determination of a new calibration curve.

6.4 Sensitivity — limit of detection

EXAMPLE

Sensitivity (S): slope of the linear part of the calibration curve

expected sensitivity S = 80 cps/% (counts per second per %).

Limit of detection for a confidence level of 3σ ($LD_{3\sigma}$)

$$LD_{3\sigma} = \frac{3\sqrt{n/t}}{S}$$

where

n is the background intensity at peak position (40 cps);

t is the measuring time (100 s);

$LD_{3\sigma}$ is the oxygen content (240×10^{-6} (240 ppm)).

7 Repeatability

This procedure has been applied to nine pellets of the same fine aluminium nitride powder, with the analytical results given in Table 1.

Table 1 — Example of repeatability for nine pellets from the same aluminium nitride powder

Pellet No	Oxygen concentration (wt%)
1	1,039
2	1,037
3	1,070
4	1,044
5	1,086
6	1,069
7	1,062
8	1,049
9	1,059
$\overline{x}$ (mean value)	1,057
σ (standard deviation)	0,016
$\varepsilon = \frac{\sigma}{\overline{x}}$ (relative standard deviation)	1,55

NOTE 1 The relative error on oxygen concentration determination is

$$\pm \frac{\varepsilon t^{*}}{\sqrt{2^{**}}} \approx 2{,}5\%$$

* with 95 % confidence level (p = 0,05, n-1 = 8), the Student factor = 2,306;

** two pellets are pressed; one measurement is made on each pellet.

NOTE 2 The results obtained are not sufficient for establishing reproducibility values.

8 Test report

The report shall be in accordance with the reporting provisions of EN ISO/IEC 17025, and shall include at least following information:

a) name and address of the testing establishment;

b) date of test;

c) on each page, a unique report identification and page number;

d) customer name and address;

e) reference to this European Standard, i.e. determined in accordance with EN 725-4;

f) authorising signature;

g) any deviation from the method described, with appropriate validation demonstration, to be acceptable for the parties involved;

h) equipment used;

i) calibration procedures;

j) description of the powder (e.g. material type, manufacturer code, batch or code number);

k) relevant test parameters;

l) results of individual determinations, mean results and standard deviations;

m) comments on the test or test results.

Bibliography

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

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