SLOVENSKI STANDARD

SIST ENV 14273:2007

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Advanced technical ceramics - Ceramic powders - Determination of crystalline phases in zirconia

Hochleistungskeramik - Keramische Pulver - Bestimmung der kristallinen Phasen in Zirconiumoxid

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ICS:

81.060.30	Sodobna keramika	Advanced ceramics

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English version

Advanced technical ceramics - Ceramic powders - Determination of crystalline phases in zirconia

Céramiques techniques avancées - Poudres céramiques -
Détermination des phases cristallines dans la zircone

Hochleistungskeramik - Keramische Pulver - Bestimmung
der kristallinen Phasen in Zirconiumoxid

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

This document (ENV 14273:2002) has been prepared by Technical Committee CEN/TC 184 "Advanced technical ceramics", the secretariat of which is held by BSI.

Annex A is normative.

This Prestandard includes a Bibliography.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this European Prestandard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Prestandard specifies a method for the routine qualitative and quantitative determination of the crystalline phases (monoclinic, tetragonal and cubic) present in zirconia powders using X-ray powder diffraction.

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2 Normative references

This European Prestandard incorporates by dated or undated reference provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Prestandard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN ISO/IEC 17025   *General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:1999).*

3 Principle

The qualitative and quantitative determination of the crystalline phases present in a given zirconia powder is derived from the X-ray diffraction analysis of a representative sample of this powder.

The qualitative analysis relies on a comparison of the recorded spectrum with available reference data (e.g. ICDD-JCPDS data base).

For the quantitative analysis, two methods are used: the polymorph method and the full pattern method. The latter consists of determining scale factors by a least squares procedure involving all recorded diffraction peaks [1,2]. The former is a well-established method, details of which can be found in basic text books [3]; it relies on a comparison of the measured intensities of selected reflections from the previously identified phases.

NOTE   A third method available for quantitative analysis is the Rietveld method. This method determines the phase constitution of the sample by fitting the whole X-ray diffraction spectrum through an iterative refinement approach. This refinement can be limited to the scale factors of each phase present (i.e. the volume fraction of the phases) or can address a whole set of parameters (e.g. cell parameters, atomic positions). Although it is

recognised that Rietveld refinement is probably the most reliable method and is more and more proposed in commercial XRD packages for quantitative analysis, this method is at present beyond the scope of this Prestandard.

4 Apparatus

Data acquisition is performed using a Bragg-Brentano diffractometer. The following experimental settings are recommended:

— Copper X-ray tube;

— Precise goniometer (two-theta error $\leq 0,5°$);

— Primary soller slit with a divergence $\leq 2,5°$;

— $5 \leq$ Divergence slit $\leq 1°$;

— Receiving slit ≤ 2 mm;

— Scatter slit $\leq 1°$;

— Secondary monochromator;

— Narrow line focus.

NOTE   In those cases where the sample preparation leads inevitably to an inhomogeneous grain structure and/or composition (e.g. grains with an inhomogeneous radial phase distribution), the use of an X-ray tube with shorter wavelength, for instance, a molybdenum X-ray or silver X-ray tube, is recommended. The shorter X-ray wavelength provides a greater depth of penetration resulting in a more representative analysis in these cases.

5 Sample preparation

In order to avoid primary extinction and assure good statistics, the powder to be analysed shall have a homogeneous grain size less than 40 µm.

By an adequate sampling procedure, a representative test sample of this powder is taken and pressed into the cavity of the sample holder. Use the backfill pressing technique to obtain a flat and smooth sample surface and to reduce preferred orientation. The dimensions of the sample holder will be such that X-rays irradiating outside of the sample volume can be avoided.

NOTE   If the powder is obtained from a solid monolithic sample by comminution (e.g. using a crushing jaw in combination with a vibratory mill or alike) it is necessary to be aware that the sample preparation may affect the type and amount of the crystalline phases present and that, accordingly, the phase composition determined may be irrelevant.

6 Test procedure

Set the excitation voltage to at least 40 kV and the current intensity at the anode of the copper X-ray tube to at least 35 mA.

NOTE   If a different X-ray tube is used, change the excitation parameters accordingly.

Data acquisition is preferably performed in the step-scanning mode, the step size being set between 0,01° and 0,05° two-theta. Alternatively record the spectrum under continuous mode with an integration width of 0,01 or 0,02.

6.1 Qualitative analysis

Set the scanning range from 10 to 80° two-theta and record the whole X-ray diffraction pattern. Select a counting time such that a good peak to background signal ratio is obtained. Practically, it should be sufficiently long to obtain a $\sigma_{rel} \leq 0,02$ for the maximum peak in the range scanned. The relative standard deviation, σ_{rel}, is given by

$$\sigma_{rel} = \frac{\sqrt{N_t + N_b}}{N_t - N_b}$$

(1)

with N_t the total counts and N_b the counts of the background.

6.2 Quantitative analysis – Method A: Polymorph method

For the polymorph method collecting the data under the following specific conditions is recommended.

Define two measurements programs:

— The first, scan between 26,5 ° and 33,5 ° two-theta, with a counting time suitable for achieving a $\sigma_{rel} \leq 0,01$ on the maximum peak;

— The second, scan between 70 ° and 77 ° two-theta, with a counting time suitable for achieving $\sigma_{rel} \leq 0,02$ on the maximum peak;

6.3 Quantitative analysis – Method B: Full pattern method

For the full pattern method the X-ray spectrum recorded for the preliminary qualitative analysis shall be used.

7 Qualitative and quantitative analysis of the recorded X-ray diffraction pattern

7.1 Qualitative analysis

Use an automatic or manual search and identify the crystalline phases present according to the ICDD-JCPDS PDF reference databank.

NOTE   The following data sets are recommended, based on the present available information. However, as the ICDD-JCPDS PDF databank is regularly upgraded, for an exact analysis, updated data sets should be used.

Crystalline phase	JCPDS-PDF Nr.
Monoclinic (Baddeleyite, syn)	37-1484
Tetragonal	42-1164 or 17-0923
Cubic (pure)	27-0997
Cubic (yttria doped)	37-1307
Cubic (calcia doped)	26-0341

7.2   Quantitative analysis – Method A: Polymorph method

7.2.1   Calculation

Calculation of the integrated intensities I(h k l)_phase

The intensities $I(h k l)_{phase}$ to be used in subsequent calculation are the integrated intensities computed from fitted and separated peaks.

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NOTE 1   Due to overlapping of the peaks of different phases it is recommended for the determination of peak intensities to use a profile fitting method. The program used should incorporate a profile shape function sufficiently flexible (e.g. Pseudo-Voigt, Voigt or Pearson VII; not only Gaussian or Cauchy). Profile fitting programs are available in most of the instrumental software packages on the market. Alternatively they can be obtained from various sources [4].

NOTE 2   The use of graphical methods is in all cases discouraged.

Calculation of the intensity factors R(h k l)_phase

A reliable determination of the crystalline phase composition of the powder sample by the polymorph method requires the use of correct intensity factors values. This in turn implies a precise knowledge of the crystallographic structure of the phases present.

The recommended intensity factor values are reported in Table 1 below. For any other zirconia/stabiliser system and/or reflection, derivation of the intensity factors should be done according to equation (2) using relevant crystallographic data available from the literature.

$$R(hkl)_{phase} = \frac{LP(2\theta).p_{hkl}.|F_{hkl}|^2}{.V^2} \quad (2)$$

with $LP(2\theta)$ the Lorentz-Polarization factor, corrected if needed for the influence of the monochromator crystal, p_{hkl} the multiplicity factor of the specific reflection, F_{hkl} the structure factor and V, the volume of the unit cell. For a detailed explanation of these factors, one should refer to the "International Tables for X-ray Crystallography" [5].

Table 1 — Recommended intensity factors for selected reflections

Stabiliser	Phase	$R(h\,k\,l)$	Ref
	Monoclinic	$R(111)_m = 60,3$	
		$R(\bar{1}11)_m = 84,8$	
Yttria	Tetragonal	$R(101)_t = 194,71 - 1,2523.YO_{1.5}\text{mol}\%$	[6]
		$R(004)_t = 4,5248 - 0,091046.YO_{1.5}\text{mol}\%$	[6]
		$R(220)_t = 10,759 - 0,2252.YO_{1.5}\text{mol}\%$	[6]
	Cubic	$R(111)_c = 183,222 + 1,39054.YO_{1.5}\text{mol}\%$	[6]
		$R(400)_c = 12,6733 - 0,0321621.YO_{1.5}\text{mol}\%$	[6]
Magnesia	Cubic	$R(111)_c = 195,65 - 2,6796.MgO.\text{mol}\%$	[7]
Calcia	Cubic	$R(111)_c = 195,65 - 2,3726.CaO.\text{mol}\%$	[7]

NOTE 1   The above equations assume the stabiliser content is known, for example as a result of a preliminary chemical analysis of the powder (e.g. by X-ray fluorescence analysis).

NOTE 2   In the case in which the stabiliser amount is unknown, the stabiliser content in the tetragonal and cubic phases can be computed from the peak positions of selected reflections, provided that the latter are well determined by fitting and that any 2-theta errors (e.g. zero shift) are minimised.

Calculation of the volume fractions of the identified crystalline phases

The calculation of the crystalline phase composition requires a preliminary identification of the phases present in the specimen. Depending on the phases identified (monoclinic and cubic, monoclinic and tetragonal, cubic and tetragonal or monoclinic and cubic and tetragonal) use one of the set of equations described below.

Case 1: The mixture consists of two phases

Case 1A: Monoclinic and Cubic or Monoclinic and Tetragonal

Calculate the volume fraction of the monoclinic and of the quadratic (either cubic or tetragonal) phase using the following expressions respectively

$$f_m = \frac{k_1 X}{1 + (k_1 - 1)X} \tag{3}$$

and

$$f_{quadra} = 1 - f_m \tag{4}$$

The integrated intensity ratio X is calculated from