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Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for determination of monoclinic phase in zirconia

FDIS stage

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Foreword

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This document was prepared by Technical Committee ISO/TC 206, *Fine ~~Ceramics~~ceramics*.

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Fine ceramics (advanced ceramics, advanced technical ceramics) — — Test method for determination of monoclinic phase in zirconia

1 Scope

This document specifies a method for the qualitative and quantitative determination of the monoclinic phase present in yttria tetragonal zirconia polycrystal (Y-TZP) powders with an yttria content ~~<~~ ≤ 6 mol% using X-ray powder diffraction. This method is also applicable ~~to determine~~for determining the monoclinic phase content in monolithic Y-TZP ceramics with an yttria content of ~~<~~ ≤ 6 mol%.

NOTE For quantitative determination of the monoclinic phase present in zirconia with a higher content of yttria or ~~other~~another stabilizer (e.g. MgO, CaO~~, etc.),~~), this document can be referenced.

2 Normative references

The following ~~document is~~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/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO 20203, *Carbonaceous materials used in the production of aluminium — Calcined coke — Determination of crystallite size of calcined petroleum coke by X-ray diffraction*

3 Terms and definitions

No terms and definitions are listed in this document.

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 Principle

The qualitative and quantitative determination of the monoclinic phase in Y-TZP powder or Y-TZP ceramics is derived from the X-ray diffraction analysis of a representative sample of this powder or ceramic.

The qualitative analysis is based on a comparison of the recorded spectrum with available reference data (ICDD PDF data bank).

The quantitative analysis is based on the polymorph method.[1–4] ~~[1–4],~~ The polymorph method provides phase analysis from a small number of integrated intensities in an X-ray diffraction scan. It is adapted for the determination of the monoclinic phase in zirconia powders or zirconia ceramics.[2,5–7] ~~[2,5–7],~~ For a full analysis, including the quantitative determination of all the phases, the full pattern method as mentioned in EVN 14273:2002[1] ~~[1],~~ or the Rietveld method ~~is~~are recommended.

5 Apparatus

The usual laboratory apparatus and, in particular, the following shall be used:

~~5.1~~ 5.1 X-ray diffractometer

~~The X-ray diffractometer shall be,~~ equipped with a copper X-ray tube, a monochromator or filter for restricting the wavelength range, a sample holder, a radiation detector, a signal processor and readout. The following experimental settings are recommended:

— precise goniometer (2θ error ≤ 0,5°);

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

— divergence slit ≤1°; ≤ 1°;

— receiving slit ≤ 2 mm;

— scatter slit ≤1°; ≤ 1°;

— continuous scanning rate at ≤2°/ ≤ 2°/min or step scanning at ≤ 0,05°/05°/step.

5.2 Sample holder

The, the dimensions of the sample holder which shall be such that X-ray irradiation outside of the sample volume can be avoided. The sample holders enable packing of a pulverized sample of sufficient height to expose a level, smooth surface to the X-ray beam.

6 Sample preparation

The powder to be analysed shall have a homogeneous grain size, in order to avoid primary extinction and assure ensure good statistics. The recommended grain size is less than 40 µm. The packing techniques for the X-ray diffraction specimen holder shall be according to in accordance with ISO 20203. A representative test sample of this powder is filled 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 test surface of the bulk sample shall be clean, smooth, and without preferred orientation. If the powder is obtained from a bulk sample by mechanical or manual grinding into powder (e.g. crushing the bulk sample in a hard alloy dies, then milling in a mortar), it should be noted that the powder preparation processes can affect the type and amount of the crystalline phases. It should also be noted that grinding by diamond wheel can affect the crystallinity and microstructures of the TZP ceramic surface. The machining can induce phase transformation and asymmetrical broadening of peaks. The heat treatment of the machined samples can decrease the phase transformation.

7 Test procedure

7.1 Qualitative analysis

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. Set the 2θ scanning range from 10°10° to 80°80° and record the whole X-ray diffraction pattern. The continuous scanning mode with a rate of ≤2°/ ≤ 2°/min is recommended. Select a counting time such that a good peak-to-background-signal ratio is obtained. The recommended relative standard deviation in the range scanned, σ_{rel}, is ≤ ≤ 0,02. The relative standard deviation, σ_{rel} is given by Formula (1)[1] Formula (1) [1].

$$\sigma_{Rel} = \frac{\sqrt{N_t + N_b}}{N_t - N_b} \sigma_{rel} = \frac{\sqrt{N_t + N_b}}{N_t - N_b} \quad (1)$$

where

σ_{rel} is the relative standard deviation;

N_t is the counts for the strongest peak;

N_b is the counts for the background for the strongest peak.

The MDI Jade or X'Pert High Score Commercially available software for X-ray diffraction analysis is recommended to calculate the background for the strongest peak.

7.2 Quantitative analysis

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. Set the 2θ scanning range from 26,5°5° to 33,5°5° and record the X-ray diffraction pattern. The step scanning mode with a rate of ≤ ≤ 0,05°/05°/step is recommended. Select a counting

time such that a good peak-to-background-signal ratio is obtained. The recommended relative standard deviation in the range scanned, σ_{rel}, is ≤ 0,01.

8 Qualitative and quantitative analysis

8.1 Qualitative analysis

Use an automatic search and identify the crystalline phases present according to the ICDD database. The recommended ICDD-PDF numbers for monoclinic ZrO_2, tetragonal $Zr_{0,92}Y_{0,08}O_{1,96}$, and cubic $Zr_{0,85}Y_{0,15}O_{1,93}$ are 37-1484, 48-0024, and 30-1468, respectively.

8.2 Quantitative analysis

For the Y-TZP zirconia system with monoclinic and tetragonal phases, calculate the integrated intensity ratio using Formula (2).

$$X = \frac{I_{m,\bar{1}11}+I_{m,111}}{I_{m,\bar{1}11}+I_{m,111}+I_{t,101}} \quad (2)$$

where

X is the integrated intensity ratio;

$I_{m,\bar{1}11}$ is the integrated intensity of monoclinic phase $\bar{1}11$ reflection;

$I_{m,111}$ is the integrated intensity of monoclinic phase 111 reflection;

$I_{t,101}$ is the integrated intensity of tetragonal phase 101 reflection.

Calculate the volume fraction of the monoclinic phase using Formula (3).

$$f_m = \frac{PX}{1+(P-1)X} \quad (3)$$

where

f_m is the volume fraction of the monoclinic phase;

X is the integrated intensity ratio;

P is the intensity factor.

For Y-TZP zirconia with an yttria content ≤ 6 mol%, when the main phases are identified to be monoclinic and tetragonal zirconia, a P value of 1,311[2][3] is used in Formula (3).

NOTE In spite of an yttria content of ≤ 6 mol%, the ratio of cubic and tetragonal phases can be changeable with synthesis conditions such as temperature, time and pressure. According to Formula (3), the theoretical calculation deviation is less than 2 % by using a different P value as reported in References [2] and [3].

For the monoclinic and cubic phases system, and the multiphase system (monoclinic, tetragonal, and cubic) with yttria or other another stabilizer (e.g. MgO or, CaO), the P value is recommended as explained. P values are given in Annex A.

Calculate the mass fraction of the monoclinic phase using Formula (4).

$$w_m = \frac{\rho_m \cdot f_m}{\sum \rho_i \cdot f_i} \quad (4)$$

where

w_m is the mass fraction of the monoclinic phase;

ρ_m is the density value of the monoclinic zirconia phase;

f_m is the volume fraction of the monoclinic phase;

ρ_i is the density value of phase *i*;

f_i is the volume fraction of phase *i*.

8.3 Limitations ~~to~~of the quantitative analysis

If strong preferred orientations are present in the Y-TZP powders or ceramics, the results are not acceptable. If the zirconia phases (monoclinic, tetragonal, cubic) are overlapped with other phases in the ceramic composites containing zirconia, the results are not acceptable.

9 Test report

The test report shall be prepared in accordance ~~to~~with ISO/IEC 17025 and shall include the following information:

a) ~~a)~~ the name of the testing establishment;

b) ~~b)~~ the date of the test, report identification, number, operator and signatory;

c) ~~c)~~ a reference to this document~~,~~, i.e. ISO 5803:—;

d) ~~d)~~ powder identification, method of test specimen sampling and preparation;

e) ~~e)~~ details of the apparatus and of the experimental parameters used when recording the diffraction pattern;

f) ~~f) the~~a list of identified crystalline phases with ~~the~~a mention of the corresponding ICDD-PDF ~~data base~~database numbers;

g) ~~g)~~ the values of the integrated intensities, $I_{\text{phase,hkl}}$, used in the calculation;

h) ~~h)~~ the *P* values used in the calculation;

i) ~~i)~~ the volume fraction and ~~the~~ mass fraction for the monoclinic phase identified;

j) ~~j)~~ deviations from the specified procedures, if any;

k) ~~k)~~ any unusual features observed.

Annex A
(informative)

Recommended *P* values in different systems

A.1 Monoclinic and cubic phases system

For the two-phase system (monoclinic and cubic phases) of ZrO_2 doped with the Y_2O_3 additive or with ~~other stabilizers (~~another stabilizer (e.g. MgO ~~or~~, CaO), calculate the integrated intensity ratio using Formula (A.1)~~Formula (A.1)~~:

$$X = \frac{I_{\mathrm{m},\bar{1}11}+I_{\mathrm{m},111}}{I_{\mathrm{m},\bar{1}11}+I_{\mathrm{m},111}+I_{\mathrm{c},111}} \frac{I_{\mathrm{m},\bar{1}11}+I_{\mathrm{m},111}}{I_{\mathrm{m},\bar{1}11}+I_{\mathrm{m},111}+I_{\mathrm{c},111}} \tag{A.1}$$

where

X is the integrated intensity ratio;

~~$I_{\mathrm{m},\bar{1}11}$~~$I_{\mathrm{m},\bar{1}11}$ is the integrated intensity of monoclinic phase ~~$\bar{1}11$ reflection~~$\bar{1}11$ reflection;

~~$I_{\mathrm{m},111}$~~$I_{\mathrm{m},111}$ is the integrated intensity of monoclinic ~~phase 111~~phase 111 reflection;

~~$I_{\mathrm{c},111}$~~$I_{\mathrm{c},111}$ is the integrated intensity of cubic phase ~~111~~ 111 reflection.

Calculate the volume fraction of the monoclinic phase using Formula (A.2)~~Formula (A.2)~~:

$$f_{\mathrm{m}} = \frac{PX}{1+(P-1)X} \quad f_{\mathrm{m}} = \frac{PX}{1+(P-1)X} \tag{A.2}$$

where

f_{m} is the volume fraction of the monoclinic phase;

X is the integrated intensity ratio;

P is the intensity factor.

The P values in Reference [3~~Table A.1~~[3]] can be used~~,~~ if the stabilizer (e.g. Y_2O_3, CaO, MgO) content is known. For ZrO_2 doped with unknown Y_2O_3, the recommended P value is 1,219 (1,219 is the mean value between P~~=~~ = 1,258 for 16 mol% $YO_{1,5}$ and P~~=~~ = 1,180 for 30 mol% $YO_{1,5}$).

~~**Table A.1 — *P* values for different amount of additive in ZrO_2**~~[3]

~~Amount of additive in ZrO_2 (mol%)~~	~~*P* value~~		
	~~$YO_{1,5}$~~	~~CaO~~	~~MgO~~
~~0~~	~~1,356~~	~~1,356~~	~~1,356~~
~~2~~	~~1,343~~	~~1,319~~	~~1,315~~
~~4~~	~~1,330~~	~~1,283~~	~~1,275~~
~~6~~	~~1,318~~	~~1,248~~	~~1,236~~
~~8~~	~~1,306~~	~~1,214~~	~~1,197~~
~~10~~	~~1,294~~	~~1,180~~	~~1,159~~
~~12~~	~~1,282~~	~~1,147~~	~~1,122~~
~~14~~	~~1,270~~	~~1,115~~	~~1,086~~
~~16~~	~~1,258~~	~~1,083~~	~~1,050~~
~~18~~	~~1,247~~	~~1,052~~	~~1,014~~
~~20~~	~~1,235~~	~~1,022~~	~~0,980~~

22	1,224	0,992	0,946
24	1,213	0,963	0,912
26	1,202	—	—
28	1,191	—	—
30	1,180	—	—

A.2 Multiphase system

For the multiphase system (the mixture of monoclinic, tetragonal and cubic) of ZrO_2 doped with Y_2O_3 additive, calculate the integrated intensity ratio using Formula (A.3)Formula (A.3):.

$$X = \frac{I_{\bar{m},\bar{1}11}+I_{m,111}}{I_{\bar{m},\bar{1}11}+I_{m,111}+I_{t,t,c}} \frac{I_{m,\bar{1}11}+I_{m,111}}{I_{m,\bar{1}11}+I_{m,111}+I_{t,t,c}} \quad \text{(A.3)}$$

where

X is the integrated intensity ratio;

$I_{\bar{m},\bar{1}11}$$I_{m,\bar{1}}$ is the integrated intensity of monoclinic phase $\bar{1}11$ reflection$\bar{1}11$reflection;

$I_{m,111}$$I_{m,1}$ is the integrated intensity of monoclinic phase 111 reflection;

$I_{t,t,c}$$I_{t,t,c}$ is the total integrated intensity of tetragonal phase 101101 and cubic phase 111111 reflections.

Calculate the volume fraction of the monoclinic phase using Formula (A.4)Formula (A.4):.

$$f_m = \frac{PX}{1+(P-1)X} f_m = \frac{PX}{1+(P-1)X} \quad \text{(A.4)}$$

where

f_m is the volume fraction of the monoclinic phase;

X is the integrated intensity ratio;

P is the intensity factor.

The recommended P value is1is 1,265 (1,265 is the mean value between P= = 1,311 for monoclinic-tetragonal ZrO_2 system and P= = 1,219 for monoclinic-cubic ZrO_2 system).

