SLOVENSKI STANDARD
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Advanced technical ceramics - Monolithic ceramics - Part 2: Oxidation test

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Hochleistungskeramik - Monolithische Keramik - Teil 2: Oxidationsprüfung

Céramiques techniques avancées - Céramiques monolithiques - Partie 2: Essai d'oxydation

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Advanced technical ceramics - Monolithic ceramics - Part 2: Oxidation test

Céramiques techniques avancées - Céramiques monolithiques - Partie 2: Détermination de l'oxidation

Hochleistungskeramik - Monolithische Keramik - Teil 2: Oxidationsprüfung

This European Prestandard (ENV) was approved by CEN on 4 June 2001 as a prospective standard for provisional application.

The period of validity of this ENV is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the ENV can be converted into a European Standard.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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Foreword

This European Prestandard has been prepared by Technical Committee CEN/TC 184 "Advanced technical ceramics", the secretariat of which is held by BSI.

EN 12923 consists of two parts:

Part 1: *General practice for undertaking corrosion tests (ENV)*

Part 2: *Oxidation test (ENV)*

Annex A is informative.

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, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 SCOPE

This Part of ENV 12923 describes a simple oxidation test for advanced technical ceramics. The test is designed to give an assessment of the mass and dimensional changes of test pieces following oxidation at high temperature in an oxidizing atmosphere, and to assess whether oxidation has a significant effect on the subsequent strength, either at room temperature or at elevated temperatures.

NOTE 1 This test method does not allow definition of other mechanical performance changes resulting from high-temperature exposure, such as changes in susceptibility to subcritical crack growth, creep behaviour, migration of secondary constituents, etc.

NOTE 2 This test method does not cover the additional effects of other corrodents in the ambient atmosphere, such as salt vapours, reducing or corrosive gases, and other contaminants. This method also does not cover tests at pressures other than ambient atmospheric pressure.

NOTE 3 An interlaboratory evaluation of the procedure given in this standard is summarised in annex A.

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).

ENV 820-1 *Advanced technical ceramics –Monolithic ceramics –Thermomechanical properties – Part 1: Determination of flexural strength at elevated temperature.*

EN 843-1 *Advanced technical ceramics – Monolithic ceramics – Mechanical properties at room temperature – Part 1: Determination of flexural strength.*

ENV 1006 *Advanced technical ceramics – Methods of testing monolithic ceramics – Guidance on the sampling and selection of test pieces.*

EN 60584-1 *Thermocouples – Part 1: Reference tables (IEC 60584-1:1995).*

EN 60584-2 *Thermocouples – Part 2: Tolerances (IEC 60584-2:1982+A1:1989).*

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

ISO 3611 *Micrometer callipers for external measurement.*

ISO 4677-1 *Atmospheres for conditioning and testing – Determination of relative humidity – Part 1: Aspirated psychrometer method.*

ISO 4677-2 *Atmospheres for conditioning and testing – Determination of relative humidity – Part 2: Whirling psychrometer method.*

ISO 6906 *Vernier callipers reading to 0.02 mm.*

3 TERMS AND DEFINITIONS

For the purposes of this European Prestandard the following terms and definitions apply.

3.1
oxidation
process of reaction of a ceramic material with oxygen in the surrounding atmosphere, including any internal reactions as a result of the presence of open porosity or of diffusion of ions to or from the ceramic surface

3.2
catastrophic oxidation
oxidation of a ceramic material which, under prescribed conditions leads to rapid material destruction as a result of lack of development of protective surface layers, skins or scales

4 BACKGROUND

Non-oxide ceramic materials, such as those based on silicon nitride, silicon carbide, titanium diboride and boron nitride, are subject to chemical change when exposed to oxygen in ambient atmospheres at high temperatures. The changes are generally the substitution of the non-oxygen nonmetallic species by oxygen, which results in a mass change and the development of a surface skin of altered composition. In addition, the chemical potentials involved can cause migration of both metallic and nonmetallic species within the near surface layer, altering the microstructure of the material. In the case of materials with open porosity, such as reaction-bonded silicon nitride and some silicon carbides, oxidation will generally occur through continuous pores which are initially surface connected, although these may become blocked as oxidation proceeds. There may be a consequent gradient of the extent of oxidation through the thickness of a sample or component.

The extent of oxidation is controlled by the chemical nature of the material, its homogeneity and the distribution of any adventitious impurities. Local concentrations of impurities or pores intersected by the surface of the test piece, for example, may lead to locally enhanced oxidation and the formation of oxidation pits.

The nature of the external surface of the test piece will change. In some cases a glazed appearance may result if the oxidation products are glassy in character, such as in the case of some silicon nitrides and silicon carbides. In others where the surface layer becomes substantially crystalline, it may be matt in appearance. Such layers may be protective of further oxidation, or substantially slow the process down if they remain intact. However, in some cases, the oxidation product may not adhere to the sample, but tend to flake off as a result of disruptive forces caused by volume changes, phase changes and/or thermal

expansion mismatches and/or thermal cycling. In extreme cases, the oxidation layer becomes non-protective, and oxidation becomes catastrophic leading to complete disruption of the material. This may apply particularly to some silicon nitride products when tested in the intermediate temperature range, typically 800 °C to 1000 °C.

Such chemical and microstructural changes may lead to significant variations in mechanical properties. In particular, the nature of strength-determining defects may alter, especially if they are located at or near the surface of test pieces. Full determination of such changes is beyond the scope of this Prestandard, which is limited in scope to determination of variations of mass, dimensions and room temperature or elevated temperature strength. These have relevance to the screening of general material behaviour, and to the mechanical performance of components which are heated and cooled, and are expected to maintain mechanical integrity at ambient temperature.

5 INTERFERENCES

5.1 Mass change

5.1.1 Accurate determination of mass changes relies on minimal contact between the test piece and the apparatus in which it is housed for the duration of the oxidation test. If strong reaction occurs between the test piece surface and its support, a significant error in registered mass change may result.

5.1.2 It is recognised that the oxidation reaction at edges or corners of test-pieces may be modified at these points, and thus the overall mass change per unit nominal area may not be representative of flat or gently curved surfaces alone. The effect may be minimal for oxidized layers of a few micrometres thickness, but becomes increasingly significant for thicker layers. In materials which oxidize internally as a result of containing open porosity, the calculation of mass change per unit nominal surface area may be influenced by the cross-sectional shape of the test piece. Results from this test method may not be directly applicable to the behaviour of components of different shape. However, they may provide a broad comparison of behaviour between different materials when using test pieces of the same size and geometry.

5.1.3 Free circulation of the test atmosphere is required. If this is for any reason significantly reduced by the geometrical arrangement of test pieces and supporting apparatus, rates of oxidation may be reduced.

5.1.4 It should be noted that oxidation behaviour may be influenced by the moisture and oxygen contents of the atmosphere. It is important to maintain the agreed atmospheric conditions for the duration of the test.

5.1.5 Accurate measurement of mass of small test-pieces may be limited to ± 0.05 mg, which defines also the limits of determining whether oxidation has taken place. For mass changes of this order of size or smaller it is necessary to consider using large test-piece areas.

5.1.6 The loss of material from the test-piece by spallation or even evaporation may occur. If spallation is suspected, means should be provided to collect the spallation product from each test-piece, but this may not always be possible.

5.2 Strength change

The specification EN 843-1 for flexural strength testing may not be achievable after oxidation if surfaces become rough or uneven during oxidation. The correct alignment function of the test jig may be interrupted. Such effects cannot at present be quantified. It is recommended that the alignment of the test-piece and the test jig is checked after a small pre-load is applied to the test-piece but before testing to fracture.

If the roughness of the oxide scale causes a problem, attempts can be made to flatten the immediate surface using a hard wooden or soft metal spatula, the intention being to crush asperities without damaging the underlying dense adherent oxide layer or the remaining ceramic material. Any such actions must be reported described in the report.

5.3 Dimensional changes

Measurement of true test piece dimensions after oxidation may be uncertain due to the formation of rough layers, loose scale or loss of scale. This measurement is appropriate for materials which retain coherent oxide scales.

External dimensional measurement using a micrometer or travelling microscope may not be reliable, particularly if the thickness of the oxide layer is less than 0,03 mm, or the morphology is rough. If oxide layer or reaction zone thickness is required under such circumstances, consideration should be given to examination of polished cross-sections of the oxidized test pieces.

5.4 Oxidation period

Oxidation rates may be initially very rapid and slow down as a protective skin develops. A steady-state condition may take more than 100 h to attain, and this situation may never be achieved, especially at relatively low temperatures. The oxidation period may therefore have some uncertainty as a result of the heating and/or cooling time required by the furnace system. The nominal agreed period is that while at constant temperature. However, the oxidation behaviour determined by the test may be influenced significantly by the period at lower temperatures during heating or during cooling. For example, it is recognised that reaction-bonded silicon nitride oxidizes internally by diffusion into open porosity below about 1200 ^{o}C, but the surface tends to seal at higher temperatures. Such factors need to be taken into account in the report. In the absence of specific prior knowledge of the test material, and unless the short-term behaviour is specifically required, it is advisable to heat to the test temperature quickly and to use test durations of at least 100 h, preferably at least 200 h, at the required test temperature.

Subject to agreement between parties, this test may be performed under controlled thermal cycling conditions. The results obtained from such tests may be significantly different from those under steady oxidation conditions, especially if surface oxide layers undergo cracking or spalling.

5.5 Surface quality

The oxidation behaviour of an as-manufactured surface may be different from that of a machined surface, e.g. as occurs with reaction-bonded silicon nitride. It is important to define the surface finish of test pieces used for the tests.

6 APPARATUS

6.1 High temperature furnace

6.1.1 Any suitable furnace may be employed for this test. The furnace chamber shall have an inlet for a sufficient supply of oxidizing gas (see 8.1.3) to ensure that the atmosphere does not stagnate and become oxygen deficient.

6.1.2 The temperature shall be capable of being raised to that required for testing at a minimum of 5 °C min^{-1}, of being controlled to better than ± 5 °C at all oxidation temperatures, and of being cooled at more than 5 °C min^{-1} to below 800 °C.

6.1.3 Before commencing oxidation tests, under the agreed conditions of temperature and environment, the furnace chamber shall be baked out using the same atmosphere as proposed for testing and at a temperature at least as high as the intended oxidation test temperature for a period of at least 10 h to remove contaminants.

6.1.4 If required by the agreed conditions of the test, a flowmeter and/or moisture meter in accordance with ISO 4677 shall be used to monitor the gas flow conditions.

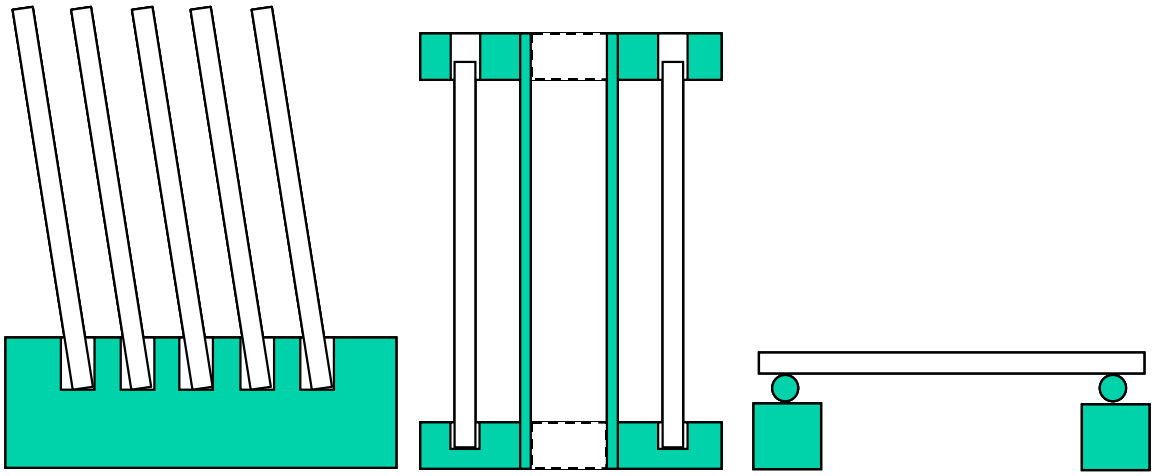
6.2 Test piece support

The test pieces shall be supported using techniques which minimise contact area, degree of adhesion and extent of reaction with the test piece (see Figure 1). Preferably this should be done using point or line contact only. Any contact of the supports with the regions of the test piece surfaces to be subjected later to loading roller contact in flexural strength testing shall be avoided. In addition, any contact with the test piece surface between the outer roller positions on the test piece when flexurally tested shall be avoided. Examples of suitable support methods include horizontal support on small diameter platinum wires, either suspended or resting on a clean non-reactive ceramic surface, or the use of a block with drilled holes no more than 3 mm deep such that the test pieces can stand near vertically with a minimum of end and edge contact.

NOTE 1 It may be necessary to perform some preliminary assessments to ensure that the supporting material is sufficiently non-reactive to play an insignificant role in determining mass change.

NOTE 2 For silicon nitride materials, platinum wire or silicon carbide particles are preferred as the contact material. Alumina should be avoided. For high-additive materials, such as sialons, mullite may be the most appropriate material. For dense silicon carbide ceramics alumina or silicon carbide contact materials may be used. Platinum is inappropriate for non-oxide ceramics containing free metallic species, such as silicon carbide containing silicon.

NOTE 3 For materials which are suspected of giving oxidation layers which might spall, the test piece support might usefully incorporate a plate or tray to catch any loose debris. The geometry and size of the tray should not reduce the circulation or air around the test piece.



(a) (b) (c)

Figure 1 - Examples of support systems for flexural strength test-pieces showing: (a) a refractory block with appropriate-sized holes in it, suitable for muffle furnaces; (b) a support system based on tubes and discs with holes, suitable for vertical tube furnaces; (c) a pair of supported parallel rods spaced near the ends of the test-pieces and with an adequate gap underneath, suitable for a muffle furnace.

6.3 Oven

For drying the test pieces, an electric oven capable of maintaining a temperature of 120 °C ±10 °C.

6.4 Chemical balance

A chemical balance with a sensitivity of at least 0,05 mg and having an accuracy of this level or better.

6.5 Micrometer

A micrometer capable of measuring to the nearest 0,01 mm in accordance with ISO 3611.

6.6 Vernier callipers

Vernier callipers measuring to the nearest 0,02 mm in accordance with ISO 6906.

6.7 Thermocouple

Type R or type S thermocouple in accordance with EN 60584-2.