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Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of oxidation resistance of non-oxide monolithic ceramics

Céramiques techniques — Détermination de la résistance à l'oxydation des céramiques monolithiques

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 20509 was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of oxidation resistance of non-oxide monolithic ceramics

1 Scope

This International Standard describes the method of test for determining the oxidation resistance of non-oxide monolithic ceramics, such as silicon nitride, Sialon[1)] and silicon carbide at high temperatures. This International Standard is intended to provide 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. This test method may be used for materials development, quality control, characterization, and design data generation purposes.

2 Normative references

The following referenced documents are indispensable for the application 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 3611:1978, *Micrometer callipers for external measurement*

ISO 6906:1984, *Vernier callipers reading to 0,02 mm*

ISO 7500-1:—[2)], *Metallic materials — Verification of static uniaxial testing machines — Part 1: Tension/compression testing machines — Verification and calibration of the force-measuring system*

ISO 14704:2000, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Test method for flexural strength of monolithic ceramics at room temperature*

IEC 60584-1:1995, *Thermocouples — Part 1: Reference tables*

IEC 60584-2:1989, *Thermocouples — Part 2: Tolerances*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
oxidation resistance
resistance against oxidation of a non-oxide ceramic material due to reaction 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
flexural strength
maximum nominal stress at fracture of a specified elastic beam loaded in bending

1) Sometimes written SiAlON is the acronym for a ceramic that contains silicon, aluminium, oxygen and nitrogen.

2) To be published. (Revision of ISO 7500-1:1999)

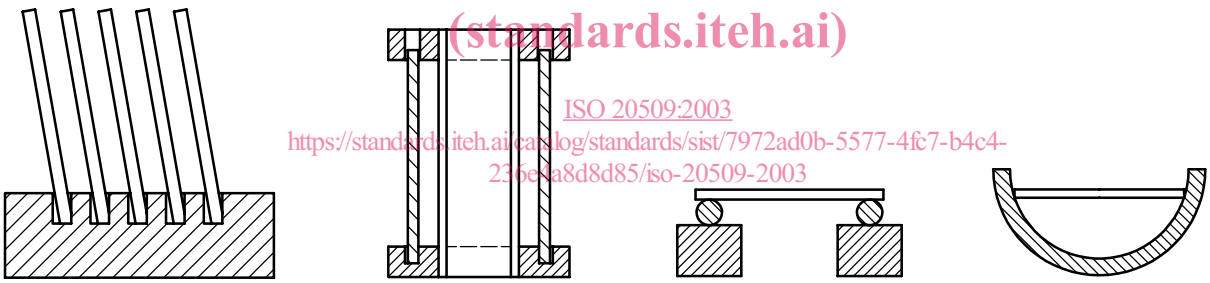
4 Apparatus

4.1 High temperature furnace, e.g. any suitable air atmosphere furnace with a nominal temperature capability of at least 1 500 °C.

The furnace chamber shall have an inlet for a sufficient supply of oxidation gas to ensure that the atmosphere does not stagnate and become oxygen deficient. 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. Before commencing oxidation tests, 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 in order to remove contaminants.

4.2 Support or supporting stand, for oxidation tests.

The test pieces shall be supported using techniques that minimize 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. Examples of suitable support methods include 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. The samples can also be situated on horizontal supports on rollers of silicon carbide or mullite, on small diameter platinum wires, either suspended or resting on a clean non-reactive ceramic surface, or on semi-rings which can be cut from ceramic tubes (alumina, mullite, silicon carbide, or silicon nitride).



a) **b)** **c)** **d)**

a) a refractory block with appropriate-sized holes in it, suitable for muffle furnace;

b) a support system based on tubes and discs with holes, suitable for vertical tube furnace;

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;

d) a test-piece supported by its ends on a ceramic semi-ring.

Figure 1 — Examples of support systems for flexural strength test pieces

NOTE 1 It may be necessary to perform some preliminary assessments to ensure that the supporting material is sufficiently non-reactive as to not significantly contribute to the mass changes in the sample.

NOTE 2 Candidate materials for supporting test pieces include silicon carbide, mullite, platinum wire and alumina. Silicon carbide and mullite may be the most suitable materials. Alumina may react with test pieces, and platinum is inappropriate for non-oxide ceramics containing free metallic species, such as silicon carbide containing silicon.

4.3 Oven, capable of maintaining a temperature of 105 °C to 120 °C.

4.4 Testing machine for flexural strength, capable of applying a uniform crosshead speed. The testing machine shall be in accordance with ISO 7500-1:— Class 1 with an accuracy of 1 % of indicated load at fracture.

4.5 Testing fixture for flexural strength, of three- or four-point flexure configuration in accordance with 5.2 of ISO 14704:2000. The recommended fixture is fully articulated and of the four-point-1/4 point configuration with the two outer bearings at a distance of 40 mm. The corresponding total length of test piece is $\geqslant$ 45 mm.

4.6 Micrometer, such as shown in ISO 3611:1978 but with a resolution of 0,002 mm for measuring the test piece dimensions. The micrometer shall have flat anvil faces such as shown in ISO 3611:1978. The micrometer shall not have a ball tip or sharp tip since these might damage the test piece. Alternative dimension measuring instruments may be used provided that they have a resolution of 0,002 mm or finer.

4.7 Vernier calliper, with a resolution of 0,05 mm or finer for measuring the length of the test piece, in accordance with ISO 6906. Alternative dimension measuring instruments may be used provided that they have a resolution of 0,05 mm or finer.

4.8 Balance, capable of weighing up to 200 g with a sensitivity of at least 0,05 mg.

4.9 Thermocouple, of type R or type S in accordance with IEC 60584-2, permitting the use of the calibration table given in IEC 60584-1.

5 Test pieces

If the strength changes are to be determined, flexural strength test pieces in accordance with Clause 6 of ISO 14704:2000 shall be used. The standard test specimens shall have cross-sectional dimensions of 3,00 mm $\pm$ 0,20 mm thickness and 4,00 mm $\pm$ 0,20 mm width. The length shall be more than 35 mm for 30 mm test fixtures or more than 45 mm for 40 mm test fixtures. All the surfaces shall be machined, and edges shall be rounded or chamfered. Any machining procedure and the surface quality of the test pieces shall be reported. The minimum number of test pieces shall be 10 for each oxidation condition to be tested, plus 10 test pieces as an unoxidized control. Means shall be taken to identify individually, similar test pieces, but shall not be marked or scribed in a way that might affect the result of the test. If strength changes are not to be determined, any test piece, in terms of size and shape, may be used.

Test pieces shall be clean and free from preparation residues and contamination due to handling which can influence the initial mass measurement and/or the oxidation rate. The test-piece cleaning procedure shall be stated in the report.

For materials with no significant open porosity and contaminated by handling, and/or by mounting or machining coolant residues, submerge the test-pieces in ethanol in an ultrasonic bath and agitate for at least 10 min. In order to avoid damage, test pieces shall not be allowed to contact either each other or a hard surface during this operation. For materials containing open porosity, internally entrained organic residues can be removed only by heating in air. The maximum temperature to which this should be done will depend on the material type, but typically a temperature of 500 °C to 600 °C for a least 1 h is required to oxidize carbonaceous residues. Material with intentionally present free carbon shall be treated at a maximum temperature of 350 °C to avoid oxidation.

6 Test procedure

6.1 Measurements of dimensions and mass of specimens

For flexural strength test pieces, measure the width, b, and thickness, h, of each test piece at several places using the micrometer (4.5) with a resolution of 0,002 mm. Measure the overall length, L_T, with the vernier callipers (4.6) with a resolution of 0,05 mm. For other shapes of test piece, measure relevant dimensions at several different places (e.g. diameter and thickness of a disc). Wash and degrease the test pieces (see Clause 5). Place in the oven (4.3) and heat to a temperature of 105 °C to 120 °C until their mass is constant. Remove and store in a desiccator. When cooled to room temperature, weigh each test piece to the nearest 0,05 mg using the balance (4.7). Store in the desiccator until tested.

6.2 Baking out in the oxidation furnace

Unless used for a similar measurement immediately prior to the test, pre-condition the furnace (4.1) and the test piece support system (4.2) at a temperature similar to or greater than that intended for the oxidation test under the intended flowing gas atmosphere. The maximum temperature shall be maintained for at least 10 h.

6.3 Oxidation test

6.3.1 Materials with high oxidation resistance

6.3.1.1 Place the test pieces on their supports (4.2) in the centre of the hot zone of the furnace (4.1) ensuring sufficient space between test pieces and their supports for adequate circulation of air. Ensure that contact with supports is minimized (see Figure 1). The contacts shall always be at locations outside the outer span used for the flexural test. The minimum spacing between test pieces as well as that between a test piece and furnace furniture shall be 5 mm.

NOTE 1 It is preferred that each batch of a least 10 test pieces per oxidation condition is exposed at the same time in the same facility. Separated exposure at separate times may result in slightly different results.

NOTE 2 The minimum spacing between components or test-pieces under test should be increased with increasing component or test-piece size to ensure unimpeded gas flow between neighbouring oxidizing surfaces.

6.3.1.2 Position a type R or type S thermocouple (4.8) in accordance with IEC 60584-2 adjacent to the test pieces for the purposes of monitoring test piece temperature during the oxidation period. Close the furnace.

6.3.1.3 Supply the oxidizing gas at a rate sufficient to provide atmosphere circulation within the furnace cavity and around the test pieces such that stagnation and oxygen depletion is avoided, but not at such a rate that results in inhomogeneous or fluctuating furnace temperature. For testing in normal air, a natural flow of the air through the furnace cavity shall be facilitated. Note that a gas flow rate is recommended of between typically 0,5 and 50 volume changes per hour, but not less than 0,1 changes per hour.

6.3.1.4 Heat the furnace to the test temperature as indicated by the measuring thermocouple adjacent to the test pieces. Maintain this temperature to within 5 °C for the required oxidation period. Cool the furnace at the maximum rate of cooling of the furnace and carefully remove the test pieces from their supports and place in a desiccator. To avoid contamination, do not touch the test pieces with naked fingers until after the final weighing. Ensure that loose deposits on the test piece surface are retained intact as far as possible.

6.3.2 Materials with low oxidation resistance

The procedure outlined in 6.3.1 can be also used in the testing of materials with low oxidation resistance or those producing low melting oxidation products, such as B_2O_3 formed during the oxidation of borides. Some modifications are suggested for the samples that react significantly with or stick to the support fixture. In these cases, it is recommended to use a system supporting each individual sample, such as the semi-rings [Figure 1 d)], so that the sample and the support can be weighed together before and after the test.

Additionally, the samples should be inserted into a furnace, preheated to the test temperature, and then air-quenched after the test to retain the high temperature condition of the surface layer for room temperature microscopic evaluation. Nevertheless, the quenching of the samples can affect the strength as a result of thermal shock.

6.4 Selecting test conditions

Test conditions (temperature, atmosphere, duration, etc.) shall be selected according to the technical requirements for undertaking the test and on agreement between parties.

NOTE 1 The test condition recommended for silicon nitrides and Sialons is 1 300 °C for 100 h or 200 h, and that for silicon carbides and advanced grades of silicon nitrides is 1 400 °C for 100 h or 200 h. Such conditions provide a means of readily distinguishing performances of similar materials.

NOTE 2 The oxidation behaviour of other non-oxide ceramics (such as borides, carbides, nitrides and silicides) varies widely, and the test conditions should be selected on the basis of preliminary experiments. Test results should be documented carefully in the report.

6.5 Measurements of mass and dimensional changes

Weigh the test pieces individually with their adherent oxidation products to the nearest 0,05 mg. Weigh any loose spallation products separately. If spallation products from individual test cannot be weighed separately, weigh them altogether. If appropriate, remeasure the external dimensions of the test pieces for the determination of dimensional changes.

NOTE It is generally not realistically possible to measure spallation that is adherent to or reacting with furnace or test piece support parts.

6.6 Measurements of flexural strength

Measure the flexural strength of the oxidized and the control test pieces in accordance with Clause 7 of ISO 14704:2000. If the nature of the oxidized surface has to be changed in order to undertake the strength tests this must be mentioned in the report.

NOTE 1 A fully articulating fixture should be used for flexural strength measurements of the oxidized specimens because they may not meet the parallelism requirements given in ISO 14704 for use of a semi-articulating fixture.

NOTE 2 A semi-articulating fixture may be used if the parallelism requirements are satisfied. One surface of an as-oxidized part may be machined to help minimize twisting or warping effects. The machined surface should be placed in contact with the inner bearings (specimen compression side) during testing.

6.7 Particular features

Record any particular features associated with the condition of the oxidized surfaces, the appearance of fractured cross-sections, etc.

NOTE Phase analysis of the oxide layer using an X-ray diffraction technique and microstructure observation of the oxide layer in the cross section using scanning electron microscopy may be useful characterization methods.

7 Calculations

7.1 Flexural strength

If flexural strength has been measured, compute the flexural strength using the relevant formula for the jig type, whether three-point or four-point bending, as in ISO 14704. Compute the average strength and standard deviation for the control batch and for each oxidation condition. Report the outer and inner spans and whether semi-articulating or fully articulating.

7.2 Mass change

If the mass change is required, compute the mass change per unit nominal surface area of test piece (C) in accordance with the formula:

$$C = \frac{W_f - W_i}{A} \quad (1)$$