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Fine ceramics [advanced ceramics, advanced technical ceramics] — Determination of corrosion resistance of monolithic ceramics in acid and alkaline solutions

Céramiques techniques — Détermination de la résistance à la corrosion des céramiques monolithiques dans des solutions acides et alcalines

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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 17092 was prepared by Technical Committee ISO/TC 206, *Fine ceramics*.

Fine ceramics [advanced ceramics, advanced technical ceramics] — Determination of corrosion resistance of monolithic ceramics in acid and alkaline solutions

1 Scope

This International Standard describes the test method for determining the corrosion resistance of fine ceramics in acid and alkaline solutions, such as sulfuric acid and sodium hydroxide. This International Standard is designed to provide an assessment of the mass changes and dimensional changes of test specimens following the corrosion test immersed in the corrosive liquids, and to assess whether corrosion has a significant effect on the subsequent strength. This test method may be used for development of materials, quality control, characterization, and design-data generation purposes.

NOTE The units and numerical values given in { } in this standard are based on traditional units and are appended for information.

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, *Micrometer callipers for external measurement*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4287, *Geometrical Product Specifications (GPS) — Surface texture: Profile method — Terms, definitions and surface texture parameters*

ISO 6353-2, *Reagents for chemical analysis — Part 2: Specifications — First series*

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

ISO 7500-1, *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*

3 Terms and definitions

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

3.1
corrosion resistance
resistance against corrosion of fine ceramic material due to reaction with corrosive species in the surrounding environment, including chemical reactions at grain boundaries and secondary phases

3.2
flexural strength
maximum nominal stress at fracture of a specified elastic beam loaded in bending

4 Apparatus

4.1 Corrosion testing apparatus, for example, any suitable apparatus capable of maintaining the test solution in a quiet boiling state and also maintaining the test solution at a constant concentration

The test container shall be made of glass or polytetrafluoroethylene, and shall have a capacity of about 1 litre. The test container should be connected to a glass vertical-type condenser, having a sufficient cooling area, by a tapered ground joint. The test apparatus shall be equipped with a thermometer for monitoring the solution temperature. Since the severe boiling state may cause mechanical damage to test specimens, the "quiet boiling state" is preferable.

NOTE 1 A device, such as a basket or a system of suspension wires resistant to the corrosive medium, may be used to prevent contact between test specimens, and to raise them off the bottom of the vessel.

Alternatively, the test specimens may be placed in a PTFE-lined chemical digestion vessel with the reagent, sealed and heated to the required test temperature. If this approach is employed, it shall be recorded in the test report.

NOTE 2 "Quiet boiling" refers to the level of bubble (vapour) formation in the liquid at a low enough level and frequency to eliminate movement of the test specimen.

4.2 Drying device, for example an oven, capable of achieving constant mass of the test specimens by maintaining a temperature of 105 °C to 120 °C.

4.3 Testing machine for flexural strength, capable of applying a uniform crosshead speed. The testing machine shall be in accordance with ISO 7500-1, with an accuracy of 1 % of the indicated force at fracture.

4.4 Test fixture for flexural strength, of three- or four-point flexure configuration in accordance with 5.2 of ISO 14704:2000.

NOTE 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 the test specimen is 45 mm or more.

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

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

4.7 Balance, with a sensitivity of at least 0,1 mg.

5 Test solutions

Sulfuric acid or sodium hydroxide solution is used for the test solution. For sulfuric acid solution, prepare the solution of 3 mol/l {6 N} concentration with guaranteed reagent as specified in ISO 6353-2, and distilled water or demineralized water as specified in ISO 3696. For sodium hydroxide solution, prepare the solution of 6 mol/l {6 N} concentration with guaranteed reagent as specified in ISO 6353-2 and distilled water or demineralized water. For solutions other than sulfuric acid and sodium hydroxide, prepare the solution of which the concentration becomes 3 mol/l. It is recommended to use the solution volume of 0,5 litre for each corrosion test.

SAFETY PRECAUTIONS — Appropriate safety precautions must be employed when preparing and handling these solutions.

6 Test specimens

The test specimen for the corrosion test shall be prepared in accordance with Clause 6 of ISO 14704:2000. The standard test specimens shall have cross-sectional dimensions of 3,00 mm ± 0,20 mm thickness, and 4,00 mm ± 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 the surface roughness shall be not more than 0,2 µm*R*a as defined in ISO 4287. Edges shall be rounded or chamfered. Any machining procedure and the surface quality of the test specimens shall be reported. The minimum number of test specimens shall be 10 for each corrosion condition to be tested, and at least 10 test specimens shall be used for flexural strength measurements before the corrosion test. Means shall be taken to identify individually similar test specimens, 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 specimens in terms of size and shape may be used.

NOTE A graphite pencil mark may be a suitable means of marking test specimens of most types.

7 Test procedure

7.1 Measurements of dimensions and mass of specimens

Measure the width (b) and thickness (h) of each test specimen 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 specimen, measure relevant dimensions at several different places (e.g. diameter and thickness of a disc). Wash and degrease the test specimens. Place in the oven (4.2) 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 to the nearest 0,1 mg using the balance (4.7). Store in the desiccator until tested.

NOTE For the majority of fine ceramics (advanced ceramics, advanced technical ceramics), the washing and degreasing conditions have little effect on the subsequent corrosion properties, and water and solvents are removed by the subsequent oven treatment. However, some materials, e.g. boron nitride or beta-alumina, may be influenced by any washing process. Care should be taken to ensure that any cleaning process used does not affect the results of the corrosion test.

7.2 Corrosion test

Heat the test container (4.1) filled with test solution to a quiet boiling state. Then place the test specimens gently on the bottom of the container and maintain the boiling state continuously for 24 h. The test specimens allowed in a single container are of the same material and the maximum number of test specimens is ten. New test solution shall be used in every test. After conducting the corrosion test, take the test specimen out from the test container, and wash sufficiently with distilled or demineralized water. Dry at 105 °C to 120 °C until constant mass is achieved, and transfer to a desiccator quickly.

NOTE Appropriate care must be taken when opening the vessel and inserting the test specimens to avoid splashing.

7.3 Measurements of mass and dimensional changes

Weigh the test specimens individually to the nearest 0,1 mg. If appropriate, remeasure the external dimensions of the test specimens for the determination of dimensional changes.

NOTE The accuracy of re-measurement of specimen dimensions will depend on the nature and extent of the corrosion, particularly the degree of pitting or of skin formation. For materials which corrode badly, it may not be possible to obtain accurate dimensional data using the micrometer. It may be more appropriate to determine a residual unaffected specimen cross-section by studying a polished cross-section by microscopy.

7.4 Measurements of flexural strength

Measure the flexural strength of the corroded and the control test specimens in accordance with ISO 14704. If the nature of the corroded surface has to be changed in order to undertake the strength tests, this shall be reported in the test report.

A fully articulating fixture (4.4) should be used for flexural strength measurements of the corroded specimens because they may not meet the parallelism requirements in ISO 14704 for use of a semi-articulating fixture.

NOTE A semi-articulating fixture may be used if the post-corrosion parallelism requirements are satisfied.

7.5 Particular features

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

NOTE Microstructure observation of the corroded layer in the cross-section using scanning electron microscopy and analysis of the corroded layer using an electron probe micro-analyzer may be useful characterization methods. Measurements of dissolved elements in test solutions may also be useful.

8 Calculations

8.1 Flexural strength

Use the appropriate calculation procedures in ISO 14704 to determine the average strength and standard deviation for the control batch and for each corrosion test. Report average and standard deviations of the strengths along with test-fixture specifics (e.g. the outer and inner spans and whether semi-articulating or fully articulating).

8.2 Mass change

Compute the mass change per unit nominal surface area of the test specimen (C) in accordance with the formula:

$$C = \frac{m_\mathrm{f} - m_\mathrm{i}}{A} \tag{1}$$

where

A is the nominal initial external surface area of the test specimen, expressed in square metres, based on initial dimensions (e.g. for rectangular test specimens, $A = 2bL_\mathrm{T} + 2hL_\mathrm{T} + 2bh$);

m_f and m_i are final and initial masses of test specimen, expressed in grams, respectively.

Compute the average result and the standard deviation for each corrosion test.

$$\overline{C} = \frac{\sum_{i=1}^{n} C_i}{n} \tag{2}$$

$$s = \sqrt{\frac{\sum\left(C_i - \overline{C}\right)^2}{n-1}} \tag{3}$$

where

$\overline{C}$ is the average value;

s is the standard deviation;

n is the total number of specimens.

NOTE The nominal surface area ignores the reduction of the true surface area by application of chamfers to the long edges of the specimen. If the guidelines on chamfer size given in ISO 14704 are followed, the error is 2 % or less, which is small compared with the other errors involved in the present measurement method.

9 Test report

The test report shall include the following information:

a) the name and address of the testing establishment;

b) the date of the test, a unique identification of the report and of each page, customer name and address, signatory of the report;

c) a reference to this International Standard, i.e. determined in accordance with ISO 17092;

d) a description of the testing condition, including the name of the acid or alkaline solution, the grade and concentration of the solution, corrosion temperature, and corrosion test time;

e) a description of the corrosion testing apparatus used, the materials used as the container, the heating method, if appropriate, the type of flexural test, etc.;

f) a description of the test material (manufacturer, type, batch number, date of manufacture, etc.);

g) a description of the details of the test specimen preparation, including nominal dimensions and surface finishing procedures, cleaning procedures, strength test conditions in accordance with the provisions of ISO 14704; in addition, a description of the details of the corrosion test, including the number of test specimens used for each corrosion test and the method of supporting the test specimens, if appropriate;

h) individual determinations of test specimen mass before and after testing, the computed mass change for each test specimen at each test condition, the mean and standard deviation for each test condition, expressed as gm^{-2};

i) individual fracture force, expressed in N, in strength tests and computed nominal fracture stress expressed in MPa (or MN m^{-2}) for each test specimen at each test condition, including the value before the corrosion test, the mean results and standard deviations for each condition;

j) any comments about the test or the results, including observations on the surface condition of the test specimens following corrosion and the corrosion layer, such as scanning electron micrographs of the corroded layer, dissolved elements from the corroded layer and thickness of corroded layer, on whether the surface condition was modified in order to conduct strength tests, and on the appearance of fracture surfaces.

Annex A
(informative)

General information

Ceramic materials are often used in severe environments such as acid and alkaline solutions since they have excellent corrosion resistance. While the corrosion of ceramics usually occurs as a result of chemical reaction, most of the reaction occurs locally at grain boundaries and the involved secondary phases.

Mass change is a common measure to evaluate corrosion resistance, because the reactant materials are dissolved in solution. Another measure of corrosion resistance is the strength variation, since the strength-determining flaw can be altered by the generation of corrosion-induced flaws. Therefore, corrosion resistance is often evaluated by both mass and strength variations.

Since corrosion of ceramics in acid and alkaline solutions usually occurs at grain boundaries and the involved secondary phases, the corrosion resistance strongly depends on the chemical composition of grain boundary phase [1-7]. Silicon nitride ceramics are typical examples of grain boundary corrosion, and develop corrosion layers inside the test specimens [1-5, 7-14], although the grain of silicon nitride itself, as well as the grain boundary, corrodes easily in HF and alkaline solutions [2, 12, 15].

The kinetics of corrosion normally exhibit a linear dependence on time in short periods while several kinds of formulas have been proposed for the kinetics of the entire corrosion process [4, 5]. The representative formula for mass loss due to corrosion is expressed as the sum of two terms in proportion to t and $t^{1/2}$. These terms originate from the interfacial-controlled dissolution of grain boundary phase and the diffusion-controlled mass transport of the leached component through the corrosion layer, respectively.

Generally speaking, the strength after corrosion rapidly decreases with an increase in mass loss in the initial stage of corrosion, and the further strength degradation in the region of greater mass loss is due to the formation of the corroded layer [5, 6, 13, 15]. The strength degradation in corroded specimens was observed in various ceramics, and this results from removal of residual stress on the surface and generating cracks with the same dimension as the corroded layer [12].

Annex B
(informative)

Interlaboratory evaluation of the test method

This International Standard was established based on the Japanese Industrial Standard: JIS R 1614. Therefore, noting the background for this International Standard may be useful.

B.1 Round robin for JIS R 1614

In order to establish the Japanese Industrial Standard (JIS R 1614:1993, *Testing methods for corrosion resistance of high performance ceramics*), the round robin was conducted from 1988 to 1990. The ceramic materials used in the round robin were alumina, silicon nitride, silicon carbide and zirconia. The dimensions of test specimens were 3 mm × 4 mm × 40 mm. The corrosion tests were conducted in corrosive solutions, including sulfuric acid and sodium hydroxide solutions. Mass changes were measured from the masses before and after corrosion tests. Flexural strength was measured in three-point flexure with a span of 30 mm. Corroded layers of cross-section of the specimens were observed with scanning electron microscopes. The results showed that the following occurred [10-13, 15].

a) The corrosion test of gas-pressure sintered silicon nitride with the addition of yttria and alumina was carried out in a variety of corrosive solutions, and it was revealed that the rapid decrease in the strength takes place at below 0,1 mg/cm^2 of mass loss.

b) The corrosion test of the gas-pressure sintered silicon nitride was carried out in H_2SO_4 (3 mol/l), and comparison was made between the specimens sustained in the solution and those placed at the bottom of the container. However, no significant effects were obtained.

c) The corrosion test of the gas-pressure sintered silicon nitride was carried out in H_2SO_4 solutions, and it was found that the mass and strength of the specimens gradually decreased with the time exposed for the corrosion test. The gradual decrease in strength was attributed to the growth of corroded layer in the range of the thickness of the corroded layer beyond 100 µm.

d) The mass and strength of gas-pressure sintered silicon nitride, as well as low-grade alumina, decrease with time when test specimens were corroded in boiling H_2SO_4 for 1 h, 24 h and 72 h, and this tendency was consistent among the participants. As listed in Table B.1, variations in mass and strength after corrosion are relatively small between participants B and C. Mass loss and strength degradation is, however, smaller for participant A because of a slightly lower temperature for the corrosion test. Participant A actually conducted the test at a slightly lower temperature of 90 °C, and this is slightly lower than the temperature around 105 °C of quietly boiling H_2SO_4 (3 mol/l) employed by participants B and C.