MEASUREMENT OF FLEXURAL STRENGTHS OF SOFC COMPONENTS

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ABSTRACT

For SOFCs to be handled without breakage during fabrication and stack assembly and to withstand the stresses developed during operation, it is necessary that the flexural strength of each component exceed a certain value. This paper reviews the available methods of measuring flexural strengths of ceramic plates. To determine the strength of a SOFC specimen with the same surface condition as it in use and allow a large specimen area being tested, concentric ring-on-ring flexural loading configuration is recommended. The emphasis of this paper is how to extend the standard ring-on-ring testing for bulk materials to the measurement of the flexural strength of a brittle layer in a multi-layer plate. As examples of how this method is applied, the flexural strengths of different layers in a NiO-YSZ / NiO-SDC / SDC tri-layer plate and a NiO-YSZ / NiO-SDC bi-layer plate were measured.

INTRODUCTION

Researches on SOFC materials and components have concentrated mainly on required functional properties, such as ionic conductivity and electrocatalytic activity. However, as SOFCs are being more widely incorporated into systems, it is clear that understanding their mechanical behaviour is also necessary for achieving the desired performance, reliability and durability. For SOFC components to be handled without breakage during fabrication, assembly and operation, it is necessary that the mechanical strength of each component be above a certain acceptable value (1).

Flexural strength is the maximum stress in a flexure mode that a specified plate develops at rupture, i.e. the ultimate strength of the plate in bending. A SOFC component has to have sufficient flexural strength to withstand the bending stresses developed during fabrication (e.g., caused by the mismatch of the different coefficients of thermal expansion of a multi-layer structure during high temperature co-firing), assembly (e.g., caused by rigid cell fixation with circumferential sealing material and an external normal load to ensure sufficient contact with interconnect), and operation (e.g., caused by the thermal cycling between room and operation temperature and inhomogeneous thermal loading).

In this study, we review the methods available for measuring the flexural strength of ceramic plates; then, after analyzing their suitability, recommend the appropriate method...
and present examples of how the method is applied. Emphasis is given to the measurement of the flexural strength of multi-layer SOFC components.

METHODS FOR MEASURING FLEXURAL STRENGTH

Fracture in brittle materials frequently originates at a surface, and the strength is determined by surface condition in conjunction with internal microstructure rather than by internal microstructure alone. A valid test method should permit the determination of the strength of specimens having the same surface condition they have in use and, so, should not require any machining of a type not occurring in the normal use of the material. Most SOFC components are used with as-fabricated surfaces. Therefore, a test method capable of measuring strength on specimens in this condition is needed.

Three- or four-point bending of a bar specimen with prescribed size has long been used to determine the flexural strengths of ceramics (2,3) and is the most widely used method to measure the flexural strengths of SOFC components (1,4,5). This method allows measurement of uniaxial flexural strength on a bar-shaped specimen which can be either specifically prepared or cut out from a larger specimen to obtain the required dimensions. The major disadvantage of this method is that the bend bar is susceptible to failure from edge cracks resulting from sample preparation unless extreme care is taken in the preparation. For this reason, biaxial flexure tests of disc or square-shaped specimens have gained increasing popularity for strength measurements of brittle materials. The biaxial flexure tests are not sensitive to edge failure because the stresses vanish at the specimen edges. In addition, the stress state of the two stress configurations in a biaxial flexure test can better represent the multiaxial stresses in a SOFC component arising from fabrication, assembling and operation. Therefore, a biaxial flexural strength measurement is preferred for SOFC components.

An ASTM standard test method for biaxial flexural strength of ceramic substrates was developed for determining strengths of circular disks of brittle materials in 1978 (6). In this method, a disk specimen is supported by three balls, equally spaced on a circle, and loaded with a flat piston in the center. The support on three balls ensures contact even with warped specimens. Assuming a uniform stress distribution over the flat piston, a theoretical stress analysis is available for the maximum radial and tangential stresses at the center. This method is restricted by the fact that the stress distribution under the piston is non-uniform, and there may be misalignment of specimen relative to piston end. Even if a uniform loading is achieved, when the plate deflects under the load, the initially uniform concentric loading would change to a concentric ring loading.

The ball-on-ring test developed later on (7,8) ensures a good loading. In this test, a disk specimen is supported on a ring and loaded centrally with a ball. A circular ball-bearing race with freely moving ball is usually used instead of a continuous ring support to minimize frictional stresses. Furthermore, a ball-on-three ball set-up is often used because there is no problem of assuring uniform loading over the specimen surface including warped specimens. The ball-on-ring or three ball test has the major advantages of there is minimum friction between the specimen and the jig during the loading and minimal requirements for test fixtures. In almost all calculations for the bending induced stresses in the ball-on-ring/three ball testing, the contact area between the load ball and
the specimen is approximated by a region of uniform constant stress with an effective radius. A central problem is that significant disagreement exists on how to determine the proper value of the effective radius under a certain test condition. In addition, in the ball-on-ring/three ball testing (also in the piston-on-three ball testing), the central loading generates steep stress gradients parallel to the specimen face and stresses only a very small area of the specimen. Thus, the strength measured corresponds to only the material at the specimen center.

In the ring-on-ring test, as shown in Fig. 1 (9,10), a flat disk specimen is supported by a ring and loaded with a smaller coaxial ring. The major advantage is that the area inside load ring is subjected to a maximum symmetrical and constant equibiaxial stress; thus, the entire area of the specimen inside the load ring is tested. The major disadvantage of the ring-on-ring test is that the friction generated between the load ring and the specimen causes an increase in stress under the loading ring. The higher the friction, the higher the stress increase. According to theoretical analyses (e.g., Fessler and Fricker (11)), when the coefficient of friction between the load ring and the specimen is less than 0.07, this effect is negligible. Because of the very low friction of PTFE (Teflon), static friction coefficient = 0.04 (12), thin PTFE sheets are recommended to be placed between the load/support rings and the specimen to reduce the friction effect (10). In addition, the PTFE sheets also act as compliant layers to minimize the effect of out-of-flatness of the specimen on the stress distribution. PTFE can be used at temperature up to about 250°C. For testing at elevated temperature, a material with low coefficient of friction and high temperature stability, such as graphite foil, should be used. If proper care is taken to eliminate friction and out-of-flatness effects, the flexural strength of a circular specimen in the ring-on-ring test is given by (10):

\[
\sigma_f = \frac{3P}{2\pi t^2} \left[ \left( 1 - \nu \right) \frac{D_s^2 - D_L^2}{2D^2} + (1 + \nu) \ln \frac{D_s}{D_L} \right]
\]

where \( P \) is the applied load at fracture, \( t \) is specimen thickness, \( \nu \) is Poisson’s ratio of the specimen, \( D_s \) is the diameter of support ring, \( D_L \) is the diameter of load ring and \( D \) is the diameter of the specimen.

\[\text{Figure 1: Section view of ring-on-ring test.}\]
This equation can also be used for square plate specimens. According to finite element analysis (13), the stress distribution in the central region is virtually independent of whether the overhang region is square or circular, although clearly there are differences outside the support ring diameter. When letting the effective diameter of a square plate equaling to its edge length and using Equation 1, the calculation only slightly underestimates the stresses inside the load ring on the square plate (less than 4% according to Powers et al. (14)).

This equation, however, is valid only if the deflections are small in comparison with the specimen thickness because it is based on small-displacement elastic theory which applies to specimens showing linear-elastic behavior throughout the test. When the deflection of the specimen becomes larger than the specimen thickness, membrane or stretching stresses become significant relative to the bending stresses (15). In this case, finite element analysis should be used to calculate the stresses. The deflection of the plate specimen can be calculated from (10)

\[
3P(1-\nu^2)D_L^2 \left[ \frac{D_L}{D_L} \left( 1 + \frac{(1-\nu)(D_s^2-D_L^2)}{2(1+\nu)D^2} \right) - \left( 1 + \ln \frac{D_s}{D_L} \right) \right]
\]

where \( E \) is the Young's modulus of the specimen.

MEASUREMENT OF FLEXURAL STRENGTH OF MULTI-LAYER SOFC COMPONENTS

A SOFC cell is basically a multi-layer ceramic device consisting of an anode, an electrolyte and a cathode. Sometimes, additional functional layers are added into the structure to achieve better performances. The fabrication usually involves a process such as co-firing laminated green ceramic layers to ensure strong bonding between adjacent layers. It is of practical importance to measure the flexural strengths of individual ceramic layers in a multi-layer structure. Because there is no existing method available for such measurement, in this study, we extend the ring-on-ring method and the corresponding equations discussed in preceding section for single layer plate to the measurement of the flexural strength of a ceramic layer in a multi-layer structure.

Consider an elastic plate consisting of \( n \) layers, whose total thickness, \( h_0 \), and the Young's modulus of each layer, \( E_1, E_2, \ldots, E_n \), are known. The average Young's modulus, \( \overline{E}_o \), the position of the neutral plane (where the strain is equal to zero when a pure bending moment is applied to the plate) from the surface of the top layer, \( z_{n0} \), and the stiffness of the multi-layer plate, \( I_0 \), can then be calculated in the following way (16)

\[
\overline{E}_o = \frac{1}{h_0} \int_{z=0}^{h_0} E(z)dz
\]

\[
z_{n0} = \frac{1}{h_0 \overline{E}_o} \int_{z=0}^{h_0} zE(z)dz
\]

\[
I_0 = \int_{z=0}^{h_0} z^2 E(z)dz - z_{n0}^2 h_0 \overline{E}_o
\]
In the ring-on-ring testing of a plate specimen of a homogeneous material, at a position within the center region bounded by the load ring and with a distance \( z \) to the middle plane of the plate, the radial and tangential stresses are equal and are the function of \( z \), Young’s modulus \( E \) and stiffness \( I (= E t^3/12 \) where \( t \) is the plate thickness) and the applied load \( F \). Therefore, Equation 1 can be rewritten as

\[
\sigma_r = \sigma_t = f(z, E, I, F) = \frac{F E z}{4 \pi I} \left[ (1 - \nu) \frac{D_s^2 - D_l^2}{2D^2} + (1 + \nu) \ln \frac{D_s}{D_l} \right]
\]

[6]

For a multi-layer elastic plate, if the Poisson’s ratios of all the layers are the same (Poisson’s ratios of all ceramic materials used for SOFC components are around 0.3 [17]), when the bending fracture initiates at the \( j \)th layer in a ring-on-ring testing, the flexure strength of the \( j \)th layer can be expressed by its Young’s modulus, \( E_j \), the distance of the fracture origin to the neutral plane of the plate, \( z_j \), the stiffness of the plate, \( I_0 \), and the applied load at fracture, \( P \), as

\[
\sigma_f = \frac{P E j z_j}{4 \pi I_0} \left[ (1 - \nu) \frac{D_s^2 - D_l^2}{2D^2} + (1 + \nu) \ln \frac{D_s}{D_l} \right]
\]

[7]

EXPERIMENTS

As examples of how the method can be applied, the flexural strengths of two multi-layer SOFC components were measured. The fabricating route of the first one was: tape casting a porous NiO-YSZ (8 mol% yttria-stabilized zirconia) substrate, screening printing a NiO-SDC (SmO$_1$$_2$($\text{CeO}_2$)$_{0.8}$) anode with lower porosity and smaller pore size, screening printing a dense SDC electrolyte, and finally high temperature co-firing. The fabrication details were described in our another paper in this proceedings (18). The fabricating route of the second component was: tape casting a porous NiO-YSZ substrate, spin-coating a NiO-SDC anode with lower porosity and smaller pore size, and finally high temperature co-firing. Sample diameters, thicknesses of the layers and their corresponding Young’s moduli are listed in Table 1. The NiO-YSZ substrate in the bi-layer component was more porous than the NiO-YSZ substrate in the tri-layer component, thus, its Young’s modulus was lower than that of the substrate in the tri-layer component.

Specimens were tested at ambient temperature with the ring-on-ring configuration as shown in Fig. 1. The specimen was spaced concentrically between a 6 mm load ring and a 14 mm support ring. Both rings were fabricated from hardened steel and had a tip radius of the cross sections of 1 mm. Two Teflon sheets with a thickness of 0.25 mm were placed between the specimen and the load/support rings to minimize the effects of friction and out-of-flatness. A scratch tester (REVETEST, CSEM, Switzerland) was used to apply the load to the load ring. The advantage of using the scratch tester instead of an ordinary compression machine was the utilization of the acoustic emission detector equipped with the scratch tester for detecting the cracking energy releasing from the specimen. Thus, the critical load could be determined when cracking/fracture was initiated. During the test, a constant loading rate of 200 N/min was used, and the load-
acoustic emission signal curve was recorded until the specimen broke. In order to measure the strengths of the thin layers, the multi-layer specimens were loaded with the thin layers (SDC and NiO-SDC layers of the tri-layer specimen and NiO-SDC layer of the bi-layer specimen) in tension because the bending cracking was caused by tensile stresses. Several tests were repeated for each type of specimen at identical conditions. The average value and the standard deviation of the flexural strength were then calculated.

Table 1. Thickness, diameter and Young's modulus of tested specimen.

| Sample   | NiO-YSZ / NiO-SDC / SDC | NiO-YSZ / NiO-SDC |
|----------|-------------------------|-------------------|
| Layer in sample | NiO-YSZ | NiO-SDC | SDC | NiO-YSZ | NiO-SDC |
| Diameter (mm) | 17 | 17 | | | |
| Thickness (µm) | 750-850 | 10-30 | 10-30 | 850-900 | 10-15 |
| Young's modulus (GPa) | 116 | 157 | 208 | 95 | 119 |

* Measured by depth-sensing indentation using a Berkovich diamond indenter at peak load of 30 mN.

Fig. 2 (a) shows a typical load-acoustic emission signal curve recorded during the testing of the bi-layer specimens, which indicates that, as soon as cracking initiated, the crack popped-in through the specimen thickness and the specimen broke. Fig. 2 (b) shows the recorded curve from a test of the tri-layer specimen. Before the tri-layer specimen broke, there was a small step of the detected acoustic emission signal. This indicates that after cracking initiated at the weakest layer of the three layers, the crack developed slowly, then, crack popped-in through the specimen thickness. In this case, the fracture load was the load corresponding to the small step of the acoustic emission signal.

**Figure. 2:** Recorded load-acoustic emission signal curves from the ring-on-ring testing. (a) Typical curve recorded in the testing of the bi-layer specimen; (b) A curve from the testing of the tri-layer specimen.

In order to determine at which layer the cracking is initiating, two additional ring-on-ring tests were performed to estimate the strengths of the NiO-YSZ substrate and the SDC electrolyte. In one test, a specimen of the tri-layer component was loaded with the NiO-YSZ substrate in tension. In another test, a single layer SDC specimen fabricated by uniaxial pressing and sintering was tested. The measured flexural strengths from the two tests were NiO-YSZ 123.3 MPa and SDC 249.0 MPa, respectively. Although the flexure
strength of the NiO-YSZ substrate in the bi-layer component was not measured, according to the relationships between porosity, Young’s modulus and flexural strength of porous NiO-YSZ plates with similar composition and fabricated by similar process (19), we knew that its flexural strength should be higher than 86 MPa.

Using Equations 3, 4, 5 and 7, the maximum bending-induced stresses in all the layers were calculated according to the measured fracture loads. Because the maximum bending-induced stresses in the two NiO-YSZ substrates and the SDC layer were much lower than their strengths (123.3 MPa, 86 MPa and 249.0 MPa, respectively), the cracking should initiate in the NiO-SDC anode layer of the both components. Thus, their flexural strengths, which were equal to the bending-induced stresses when cracking initiated, were determined. The values are listed in Table 2. The strengths of the two NiO-SDC anode layers, 80.4 ± 3.6 MPa and 74.6 ± 10.5 MPa respectively, should be sufficient to withstand the stresses which will develop during stack assembly without cracking. To determine if they are strong enough to survive during operation, the strengths of the anode layers after reduction in hydrogen should be measured. This will be our future work.

Table 2. Measured flexural strengths.

| Sample Layer in sample | NiO-YSZ / NiO-SDC / SDC | NiO-YSZ / NiO-SDC |
|-----------------------|-------------------------|-------------------|
| Flexural strength (MPa) | NiO-YSZ | NiO-SDC | SDC | NiO-YSZ | NiO-SDC |
| NiO-YSZ | 123.3 | 80.4 ± 3.6 | (249.0) | (> 86) | 74.6 ± 10.5 |

\( ^a \) Average value ± standard deviation from three tests; \( ^b \) Value from the single layer SDC sample; \( ^c \) Estimated according to Reference (19); \( ^d \) Average value ± standard deviation from four tests.

CONCLUSIONS

Methods of measuring flexural strengths of ceramic plates were reviewed. Among them, concentric ring-on-ring loading configuration is most appropriate for SOFC components because this method can determine the strength of a specimen with the same surface condition as it is in use and allows a large specimen area to be tested. Standard ring-on-ring testing for bulk materials was extended to the measurement of the flexural strength of a brittle layer in a multi-layer plate suitable for SOFC components. The flexural strengths of different layers in a NiO-YSZ / NiO-SDC / SDC tri-layer plate and a NiO-YSZ / NiO-SDC bi-layer plate were measured using this method.

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