Fracture strength and Weibull analysis of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ oxygen transport membranes evaluated by biaxial and uniaxial bending tests

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Title: Fracture strength and Weibull analysis of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} oxygen transport membranes evaluated by biaxial and uniaxial bending tests

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Keywords: BSCF; Fracture strength; Biaxial method; Uniaxial method; Weibull modulus

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Abstract: The present study evaluates the fracture strengths and the Weibull modulus of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) oxygen transport membranes by means of biaxial and uniaxial bending tests at both room temperature (RT) and 800 °C. The fracture strengths obtained from the biaxial bending tests are much lower than those obtained from the uniaxial bending tests while Weibull moduli (m) are similar. By utilising Weibull statistics the uniaxial strengths can be predicted from the biaxial values at both RT and 800 °C. Fracture surfaces at both RT and 800 °C show only a transgranular fracture mode. Failure origins are also determined by scanning electron microscope (SEM) based on the fractographic principles. Most defects determining the fracture strength of this particular material are found to be pores with a relatively large size.

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Materials Science & Engineering A

Title: Fracture strength and Weibull analysis of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} oxygen transport membranes evaluated by biaxial and uniaxial bending tests

Dear Prof. Marco Starink,

Thanks for your effort to arrange review of the manuscript, and also we appreciate the valuable comments given by the reviewer. In this version, we have addressed ALL of the points and revisions were made accordingly (highlighted by yellow in the revised manuscript). We wish that revision is satisfactory for publication of the paper. Please let us know if we need to make more effort in improvement of this paper.

Yours sincerely

Li Wang

Reviewer's comments

The article is sufficiently novel and interesting to warrant publication, especially the comparison of different strength characterization methods along with fractography is an advance to the current scientific literature.

The abstract reflects content and summarizes the problem, method, results, and conclusions.

1.The purpose of the study clearly outlined in the introduction and findings of prior works are discussed. However, especially since elevated temperature tests are carried out the authors should also elaborate in the introduction on the findings reported in the works by Araki et al. Mater Lett 32,2014,295-297 on the complex behaviour observed at intermediate and high temperatures and its relationship to mechanical parameters and the works by Rutkowski et al. J Membrane Sci381,2011,221-225 and J Euro Ceram Soc 31,2011,493-499 on creep behaviour and its relationship to high temperature phase stability.

Reply: The references mentioned above have been cited. The findings in those two references have been added into the Introduction (from Line 20, Page 2 to Line 2, Page 3) and highlighted in yellow.

2.The authors used linear regression to determine strength and Weibull modulus, mostly the maximum - likelihood is used, please comment. Also industrial standards suggest to use confidence intervals.

Reply: The 90% confidence interval for these two methods (linear regression and maximum likelihood method):

Linear regression $0.83m_{\text{true}} < m < 1.32 m_{\text{true}}$

Maximum likelihood $0.72 m_{\text{true}} < m < 1.30 m_{\text{true}}$

The smallest confidence interval is the one for the linear regression method, which is herewith recommended by the authors as a more appropriate evaluation method.

3.With respect to equation (7), ASTM industrial standards use a different equation for the effective volume based on the works by Salem, et al. Ceram. Eng. Sci. Proc., 24 (4), 2003, 357-364, what is the advantage of the current equation and do both equations lead to similar values?

Reply: The current equation is related to the disc-shaped samples, and both equations lead to the error less than 10%.

4.The authors accurately explain how the data were collected and there is sufficient information that the experiment can be reproduced. However, it should be added if only the cut surfaces were polished or all surfaces.

Reply: All the surfaces were ground and polished before any mechanical testing.

The above statement has been added into Line 1, Page 6 in the revised manuscript and highlighted in yellow.

5.The discussion is supported by the results and it does make scientific sense. Hence, it shows how the work resulted in an advance. However, the lower elevated temperature strength and especially also the lower Weibull modulus need further discussion, were in addition to the works mentioned above from Araki (also the works of Huang) and Rutkowski and the effect of the phase stability also the effects shown in Fig. 82 of the thesis of B. Rutkowski on temperature dependency of the fracture stress of specimens after different thermal treatments should be discussed.

Reply: For these two bending methods, both fracture strengths and Weibull modulus obtained at 800 °C are respectively lower than those obtained at RT. It has been reported by Rutkowski et al. that the interatomic distance increases due to chemical expansion associated with oxygen release at 800 °C, which should result in decreasing strength with increasing temperature. The lower Weibull modulus indicates a significantly larger scattering of fracture strengths at 800 °C. It is probably caused by the increase of the defect size during heating

due to the thermal expansion and the randomness of mechanical properties at high temperature, which results in a different flaw size distribution between RT and 800 °C. The above statement has been added from Line 16 Page 12 to Line 3 Page 13 in the revised manuscript and highlighted in yellow.

6.Please give an outlook on the meaning of the results for the application in OTM units, see for example Rutkowski et al J Membrane Sci 462,2014,69-74 and potential effects of oxygen pressure gradients, see for example Huang et al J Euro Ceram Soc 34, 2014,1777-1782. The conclusions are sound and justifiable as based on the results and discussion, but should be extended after improving the discussion.

Reply: Most defects in this particular material are found to large pores, suggesting that the use of BSCF for membrane applications required careful control of the sintering process in order to eliminate the pore coalescence or cavities. The above statement has been added from Line 8 to Line 10 Page 16 in the revised manuscript and highlighted in yellow.

The conclusion has been extended in the revised manuscript and the newly added text is highlighted in yellow.

Fracture strength and Weibull analysis of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ oxygen transport membranes evaluated by biaxial and uniaxial bending tests

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Abstract

The present study evaluates the fracture strengths and the Weibull modulus of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) oxygen transport membranes by means of biaxial and uniaxial bending tests at both room temperature (RT) and 800 °C. The fracture strengths obtained from the biaxial bending tests are much lower than those obtained from the uniaxial bending tests while Weibull moduli (m) are similar. By utilising Weibull statistics the uniaxial strengths can be predicted from the biaxial values at both RT and 800 °C. Fracture surfaces at both RT and 800 °C show only a transgranular fracture mode. Failure origins are also determined by scanning electron microscope (SEM) based on the fractographic principles. Most defects determining the fracture strength of this particular material are found to be pores with a relatively large size.

Keywords: BSCF; Fracture strength; Biaxial method; Uniaxial method; Weibull modulus

1 Introduction

Currently, mixed ion-electron conducting (MIEC) materials have been attracting great attention due to their high oxygen permeation which makes them promising candidate materials for oxygen transport[1-4]. Among these MIEC materials, perovskite-structured $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) have been of particular interest due to their 100% selective permeation in theory at elevated temperature during the operation process[5]. However, the applications of these MIEC materials are challenged not only by the high operating temperature ($\sim 800^\circ\text{C}$), but also by high oxygen pressure gradients through the materials as well as chemically induced strains[6]. Besides high oxygen permeability concerned[7, 8], the MIEC materials also need to maintain their long-term phase and structural stability because they are subjected to high temperature, complex mechanical stresses and stress cycles.

Despite the broad interest in mechanical properties, especially fracture strengths, of BSCF, at present only the biaxial bending test was used to evaluate their fracture strengths[6, 9-11]. However, the determination of fracture strength from only one method is not sufficient for design requirement. Additionally, It has been reported that the fracture strength is highly dependent on measurement techniques, because different methods have different effective volumes and stress states[12]. Previous

studies have also shown that BSCF exhibit complex behaviour in electrical, thermal and mechanical properties at high temperatures [13-16]. Therefore, it is necessary to characterise and compare the mechanical properties of this material using different testing approaches. In this way, well-designed experiments coupled with reliability analysis can optimise rational designs that ensure the successful use of ceramics in demanding structural applications[17]. The purpose of this paper is to compare the fracture strength of BSCF obtained from both uniaxial and biaxial bending tests and evaluate both tests by means of Weibull statistics. Fracture analysis is also performed in order to determine and characterise the failure origins.

2 Theory and governing equations

Because uniaxial and biaxial bending tests represent different stress states and different test volumes or surface areas, Weibull analysis is used to study this difference and determine whether it is simply an effect of loading geometry. The simplest treatment of the size dependence of strength is through the application of Weibull statistics based on the fracture theory[18]. Assuming the two-parameter Weibull distribution, the probability (F) of failure of a component is given by[19, 20]

$$F = 1 - \exp\left[-\left(\frac{\sigma_{\max}}{\sigma_c}\right)^m V_{\text{eff}}\right] \quad (1)$$

where $\sigma_{\max}$ is reference maximum stress in the stressed solid, m Weibull modulus, σ_c characteristic strength, and V_{eff} effective stress volume defined by

$$V_{\text{eff}} = \int \left(\frac{\sigma}{\sigma_{\max}}\right)^m dV \quad (2)$$

where σ is the local stress in an elemental stressed volume d_v . Equation (1) can be simplified as follows:

$$\ln\left(\frac{1}{1-F}\right) = \left(\frac{\sigma_{\max}}{\sigma_c^*}\right)^m \quad (3)$$

where the parameter σ_c^* [$\sigma_c^* = \sigma_c(V_{\text{eff}})^{\frac{1}{m}}$] represents the specific characteristic strength of the specimen at $F=0.632$; and F , the failure probability, is defined by the relation[21]:

$$F = (i - 0.5)/N \quad (4)$$

where i is the ranking number of a specimen in sample size N in increasing order of fracture stress σ . To analyse fracture strength data, Equation (3) can be rewritten as follows[21]:

$$\ln\ln\left(\frac{1}{1-F}\right) = m\ln\sigma_{\max} - m\ln\sigma_c^* \quad (5)$$

Hence, a plot of the left side of Equation (3) as a function of the natural logarithm of fracture stress should obtain a straight line with a slope of m .

Average strengths in uniaxial and biaxial bending tests are related to the effective volumes by the relation[22]:

$$\frac{\sigma_{3P}}{\sigma_{\text{ROR}}} = \left(\frac{V_{\text{ROR}}}{V_{3P}}\right)^{\frac{1}{m}} \quad (6)$$

The effective volume for the ring-on-ring test (ROR) has been given by Batdorf[23] and Breder[18]:

$$V_{\text{ROR}} = 2t\pi r_i^2 m^{0.45} \quad (7)$$

where r_i is the radius of the loading ring. The effective volume for the three-point bending test (3P) is given by [24]:

$$V_{3P} = \frac{Lhb}{2(m+1)^2} \quad (8)$$

L is the distance between the two support points, b is the width of the cross section at the applied load, and h is the thickness of the specimen. The effective volume is regarded as an assumed volume where the tensile stress is applied. Combining Equations (6), (7) and (8), the fracture strength obtained by either test method can be used to predict the fracture strength measured by the other.

3 Experimental procedure

3.1 Sample preparation

Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} powder was supplied by Treibacher Industrie AG, Austria. The powder was packed in a cylindrical stainless steel die with a diameter 28 mm, and uniaxially pressed under a pressure of 100 MPa. The as-pressed BSCF powder was then sintering at a temperature of 1100 °C for 10 hours. The heating rate and the cooling rate during the process of sintering were set to 180 °C/hour. After sintering, the diameters of the specimens shrank from 28 mm to approximately 22 mm. The as-sintered BSCF bulk were cut into disc-shaped and bar-shaped specimens using a diamond cutting blade in a precision cut-off machine (Accutom 5, Struers). The specimens were ground with SiC paper with different grit sizes from P400 to P1200, and then polished with diamond paste descending from 6 μm to the final stage of 1 μm. The disc-shaped specimens for the ring-on-ring tests had a diameter of ~ 22 mm, and thickness of ~ 1 mm. The bar-shaped specimens for the three-point bending tests

had a dimension of $\sim 2.1 \times 2.3 \times 14 \text{ mm}^3$. All the surfaces were ground and polished before any mechanical testing.

3.2 Mechanical testing procedure

Mechanical testes were carried out using biaxial and uniaxial bending tests on an Instron 5569 test machine at both RT and 800 °C in air. The load was applied within an accuracy of 0.01 N and the displacement was recorded within an accuracy of 0.001 mm. Thermocouples near the test specimens were used to monitor the temperatures of the specimens at 800 °C. 10 specimens were used for each method at RT and 800 °C, respectively. The force was applied at a rate of 100 N/min by a computer-driven load cell and a sensor was used to record the applied load and the displacement of the specimen. The peak load was used to calculate the fracture strength. Prior to the test, the testing fixtures (made of alumina) were aligned with respect to the loading nose (made of alumina) to ensure that the loading was symmetrical. For the tests at 800 °C, a heating rate and a cooling rate of 180 °C/hour were used, and a dwell time of 1 hour was chosen to reach a uniform temperature all over the sample before testing.

The ring-on-ring bending test was conducted as a type of biaxial bending tests in this work. The schematic picture of the test is shown in Figure 1:

The test conditions were in accordance with the ASTM standard C1499-05[25]. The fracture strength was calculated using the following equation:

$$\sigma_f = \frac{3P}{2\pi t_h^2} \left[(1 + \nu) \ln \left(\frac{r_2}{r_1} \right) + \frac{1-\nu}{2} \left(\frac{r_2^2 - r_1^2}{r_3^2} \right) \right] \quad (10)$$

where P is the peak load, t_h is the specimen thickness, ν is the Poisson ratio. r_1, r_2 , and r_3 are the radii of the loading ring, the supporting ring and the specimen, respectively. The values of t_h , r_1 , r_2 and r_3 are 1.0, 1.9, 8.4, 21.8 mm, respectively. Poisson ratio is taken as 0.3. The three-point bending test was conducted as a type of uniaxial bending tests to measure the fracture strength of BSCF in this work. The schematic diagram of the three-point bending test is shown in Figure 2. The calculation of the fracture strength was performed based on ASTM Standard C 1161[26] using the following equation:.

$$\sigma_f = \frac{3PL}{2bh^2} \quad (11)$$

where P is the peak load, L is the distance between the two support points, b is the width of the cross section at the applied load, and h is the thickness of the specimen. The mean values of b , h , L are 2.1, 2.3, and 8 mm, respectively.

3.3 Microstructural characterisation

The relative densities of all the BSCF specimens determined by the Archimedes method in distilled water were over 94%. The phase composition of all the BSCF was determined to be a single cubic phase by X-ray diffraction. The diameter of grain size was determined to be 22 μm using the area counting technique. Details of these compositional and microstructural features can be found elsewhere[27]. The fracture surface were analysed based on the fractographic principles[28]. The pore size was quantified by Image-Pro Plus 6.0 software based on SEM images.

4 Results

4.1 Fracture strengths and Weibull analysis

Biaxial and uniaxial fracture strengths were measured using ring-on-ring and three-point bending tests at both RT and 800 °C, respectively. The results are summarised in Table 1 which gives the specimen number (N), the mean fracture strengths and corresponding standard deviations, the coefficients of variation, the characteristic strength (σ_c), the Weibull modulus (m) and standard errors, coefficients of correlation (R^2).

Figure 3 shows Weibull plots of fracture strengths evaluated by both methods at RT and 800 °C. The Weibull modulus m and characteristic strength σ_c are determined from the slope and the intercept of the straight line fitted by linear regression, respectively, and summarised in Table 1. The biaxial strength data give $m=10.2$ ($R^2 = 0.91$) at RT and $m=5.5$ ($R^2 = 0.95$) at 800 °C, while the corresponding values for the uniaxial strength at RT and 800 °C are 9.6 ($R^2 = 0.94$) and 5.4 ($R^2 = 0.91$), respectively. The Weibull modulus obtained from the biaxial bending tests is similar to that obtained from the uniaxial bending tests at both RT and 800 °C, respectively. It suggests that there is little difference in the flaw population between these two experiments and the effective volume calculations are valid for the both room and high temperatures.

It is noted that the fracture strengths here are lower than those obtained from Huang *et*

al.[10] who have studied the strengths of BSCF between RT and 800 °C using the ring-on-ring bending test. Compared with the BSCF specimens studied in this work, the specimens used by Huang *et al.*[10] show similar porosity, but smaller grain sizes. Therefore, one possible explanation of the difference is that the defect size, which is critical to determining the fracture strength, can be related to the grain size. Another possible reason is a larger effective volume for this present experiment, which leads to smaller fracture strength according to Equation (6), although the same method is used to determine the fracture strength.

For all the specimens evaluated in this work at both RT and 800 °C, as seen in Table 1, the fracture strengths obtained by the uniaxial tests are significantly higher than those determined by the biaxial tests. This finding is consistent with the study by Shetty *et al.* [22] who have also found the strengths of alumina determined by the uniaxial bending test were higher than those obtained by the biaxial method. The discrepancy is attributed to the difference in the effective area or volume of the material subjected to maximum stress between these two tests [18]. To be more specific, by accounting for the effective volume of the materials under stress [Equations (8) and (9)] it is found that biaxial specimens ($V_{\text{eff}}=20.5 \text{ mm}^3$) are subjected to a larger effective volume than that of the three-point bending specimens ($V_{\text{eff}}=0.17 \text{ mm}^3$), which then results in a smaller fracture strength obtained by the biaxial test according to Equation (6).

The fracture strength measured by either test can be predicted by that measured by the

other using Equations (6), (7) and (8). For example, the predicted fracture strengths of the three-point bending tests are plotted in Figure 4 based on the measured fracture strengths by the ring-on-ring bending tests. The predicted strengths of the three-point bending test based on the ring-on-ring tests are only 6.3% and 10.3% lower than the measured strengths from the three-point bending tests at RT and 800 °C, respectively, as shown in Table 2. The ratios of fracture strengths measured by these two methods are also similar to those obtained from the predictions at both RT and 800 °C. This comparison suggests that the predicted approach is adequate for the present case.

For all the specimens evaluated in Table 1, it should be noted that the coefficient of variation obtained at 800 °C is twice higher than those at RT as for both tests, which may be caused by the change of defects size during heating due to the thermal expansion and the randomness of the mechanical properties at high temperature[29]. The coefficients of variation determined by the biaxial bending tests at RT and 800 °C are less than those determined by the uniaxial bending tests (Table 1). However, the standard deviations determined by the biaxial bending tests at RT and 800 °C are slightly higher, which may be attributed to the complex stress state developed and the frictional force between the contact surface[29].

Figure 5 shows the typical load-displacement curves of different testing methods at both RT and 800 °C. In the case of the same method, the failure deflection of the specimen at 800 °C is larger than that at RT. On the other hand, the load-deflection curves obtained from these two methods at RT are linear while the curves obtained at

800 °C are nonlinear. This indicates that the plastic deformation of the BSCF specimens (e.g creep) occurs at 800 °C. The nonlinear load-deflection curve was also observed in $\text{LaCrO}_{3-\delta}$ and was attributed to the formation of oxygen vacancies at high temperature[30]. Previous studies [31, 32] have also shown that BSCF materials release oxygen and form oxygen vacancies at high temperature. However, according to the load-deflection curves at 800 °C, the slopes of the curves increase with increasing deflection, suggesting an increase in deformation resistance of the material. This change could not be caused by the formation of vacancies as it would lead to a decrease in material strength. A more plausible explanation is pore closure induced by compressive stress at 800 °C, which makes the further deformation more difficult. Compared with the three-point bending tests, the deflections in ring-on-ring bending tests are larger at both RT and 800 °C due to their larger effective volume.

4.2 Fractography

It is important to study the fracture surface, fractography, which can shed light on not only the process of fracture but also failure origins. In general, fracture surfaces are often observed as transgranular or intergranular. After the ring-on-ring and three-point bending tests, the fracture surfaces of BSCF tested at RT and 800 °C are investigated by the SEM to determine the fracture modes, and the morphology of the fracture surfaces is shown in Figure 6. At both RT and 800 °C the BSCF specimens show the transgranular mode, similar to previous studies reported in the literature[10]. As shown in Figure 6(B), additional particles are observed along the grain boundaries

and in the inner part of the grains after high temperature testing. However, the XRD investigation does not give any indication with respect to the presence of other phases, probably due to the fact that the amount of these particles is too low and therefore beyond the detecting capability. The only detectable phase on the fracture surface from all the specimens is cubic BSCF. Efforts have been made to determine the compositions of the small particles using EDS. However, no difference in compositions has been found between the matrix phase and these particles. Additional work is required to unequivocally determine the composition and structure of these small particles by transmission electron microscopy in future. However, examination on the BSCF surface prepared by grinding and polishing shows no such particles (Figure 6(C)). This indicates that the particles only exist at the surface, possibly formed through the reaction between the crack surface and carbon dioxide in the air at high temperature after failure[33]. Therefore, these particles should have no influence on the measured fracture strength of BSCF at 800 °C.

5 Discussion

For these two bending methods, both fracture strengths and Weibull modulus obtained at 800 °C are respectively lower than those obtained at RT. It has been reported by Rutkowski *et al.*[13] that the interatomic distance increases due to chemical expansion associated with oxygen release at 800 °C, which should result in decreasing strength. The lower Weibull modulus indicates a significantly larger scattering of fracture strengths at 800 °C. It is probably caused by the increase of the defect size during

heating due to the thermal expansion and the randomness of mechanical properties at high temperature, which results in a different flaw size distribution between RT and 800 °C.

In order to understand the failure mechanism of BSCF upon loading, the failure origins need to be determined. As mentioned above, there is little difference in flaw distribution between three-point and ring-on-ring bending tests. In addition, compared with the examination of fracture surfaces obtained from ring-on-ring bending tests, the failure origins of the specimens broken by three-point bending tests are much more convenient to be examined. Therefore, the focus here is to find and study the failure origins of the specimens fractured by the three-point bending tests

For each case, fracture positions always initiate on or near the tensile side of the specimens. The large pores shown in Figure 7, near the tensile face, are regarded as failure origins as the pores can act as stress concentrators and lead to the failure of the specimens. This is further confirmed by the fact that the regions surrounding the fracture origins are smoother than the remainder of the surface and fracture lines emanate from the large pore as shown in Figure7 (A). Other characteristic failure origins include edge fracture and surface cracks.

Figure 8 shows the character of the failure origin of each specimen loaded by the three-point bending tests at RT and 800 °C. Fractography analysis was performed on the fracture surface of BSCF and the type of the failure origin is indicated by an arrow in Figure 7. A capital letter with an arrow refers to the character of a fracture origin; P,

E and C correspond to a pore, edge fracture and surface crack.

The fracture origins of most BSCF specimens at both temperatures were porous regions extending 40–80 μm , as exemplified from the selected fractography in Figure 7. This size is larger than the maximum defect size (56 μm) measured on the specimen surface, as shown in Figure 9(A). In addition, the pore size distributions of the specimens having the maximum and minimum fracture strength are similar, as shown in Figure 9(B). The maximum defect size (56 μm) measured is lower than the maximum pore size at the fracture origin observed on the fracture surface ($\sim 80 \mu\text{m}$). This disagreement can be ascribed to a relatively small area (1 mm^2) utilised for counting defects. According to the model proposed by Quinn[24], the effective surface area of a flexural BSCF specimen by the three-point bending test at RT in this study is calculated to be 3.62 mm^2 with a Weibull modulus of 9.6. Therefore, it is necessary to enlarge the examination area for counting defects in order to discover those critical contributions to the fracture of flexural specimens. To achieve this, the defect frequency data are extrapolated to the larger defect size region to estimate the maximum defect size possibly existing in the flexural specimens. The number of defects at a given size was recalculated per 1 mm^2 . Note that the number of defect sizes also depends on the range for counting and is normalised by dividing it by the employed counting range, 1 μm [34]. The result is shown in Figure 9(C). The defect frequency corresponding to the flexural specimen is determined to be 0.31, statistically (One defect for the effective surface areas; $1/3.62=0.28$), and the resultant defect size is 80 μm . This gives a relatively acceptable defect size, although more

detailed observations are needed for this defect frequency.

It should be noted that the fracture strength can be also determined from the relationship between the critical defect and the fracture toughness, according to the following equation:

$$\sigma_f = \frac{K_{IC}}{Y\sqrt{c}} \quad (12)$$

σ_f is the fracture strength; K_{IC} is the fracture toughness; Y is the flaw shape factor; c is the critical flaw size. According to the guidance of fractographic investigation[28], Y value of the bulk failure origin is 1.47. It has been also reported that the fracture toughness of BSCF at RT is approximately 1 MPa·m^{0.5} [35]. The fracture strength of the BSCF (81MPa) specimen shown in Figure 7(A) is similar to that (87MPa) estimated from the Equation (12).

6 Conclusion

The present study evaluates the fracture strengths and the Weibull modulus of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) materials by means of biaxial and uniaxial bending tests at RT and 800 °C. The fracture strengths obtained from biaxial bending tests at RT (73 MPa) and 800 °C (45 MPa) were lower than those obtained from uniaxial bending tests at RT (127 MPa) and 800 °C (107 MPa), respectively, because the effective volume of the former testing method is larger than the latter. The Weibull modulus obtained from the biaxial tests were similar as those obtained from the

uniaxial tests at RT and 800 °C, respectively. It suggests that there is little difference in the flaw population between these two experiments. However, the Weibull modulus obtained at 800 °C was much lower than that obtained at RT. It is probably caused by the change of defects size during heating due to the thermal expansion and the randomness of mechanical property at high temperature, which results in a different flaw size distribution between RT and 800 °C. Fracture surfaces at both RT and 800 °C show only a transgranular mode. Most defects in this particular material are found to large pores, suggesting that the use of BSCF for membrane applications requires careful control of the sintering process in order to eliminate the pore coalescence or cavities.

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Fracture strength and Weibull analysis of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ oxygen transport membranes evaluated by biaxial and uniaxial bending tests

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Abstract

The present study evaluates the fracture strengths and the Weibull modulus of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) oxygen transport membranes by means of biaxial and uniaxial bending tests at both room temperature (RT) and 800 °C. The fracture strengths obtained from the biaxial bending tests are much lower than those obtained from the uniaxial bending tests while Weibull moduli (m) are similar. By utilising Weibull statistics the uniaxial strengths can be predicted from the biaxial values at both RT and 800 °C. Fracture surfaces at both RT and 800 °C show only a transgranular fracture mode. Failure origins are also determined by scanning electron microscope (SEM) based on the fractographic principles. Most defects determining the fracture strength of this particular material are found to be pores with a relatively large size.

Keywords: BSCF; Fracture strength; Biaxial method; Uniaxial method; Weibull modulus

1 Introduction

Currently, mixed ion-electron conducting (MIEC) materials have been attracting great attention due to their high oxygen permeation which makes them promising candidate materials for oxygen transport[1-4]. Among these MIEC materials, perovskite-structured $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) have been of particular interest due to their 100% selective permeation in theory at elevated temperature during the operation process[5]. However, the applications of these MIEC materials are challenged not only by the high operating temperature ($\sim 800^\circ\text{C}$), but also by high oxygen pressure gradients through the materials as well as chemically induced strains[6]. Besides high oxygen permeability concerned[7, 8], the MIEC materials also need to maintain their long-term phase and structural stability because they are subjected to high temperature, complex mechanical stresses and stress cycles.

Despite the broad interest in mechanical properties, especially fracture strengths, of BSCF, at present only the biaxial bending test was used to evaluate their fracture strengths[6, 9-11]. However, the determination of fracture strength from only one method is not sufficient for design requirement. Additionally, It has been reported that the fracture strength is highly dependent on measurement techniques, because different methods have different effective volumes and stress states[12]. Previous

studies have also shown that BSCF exhibit complex behaviour in electrical, thermal and mechanical properties at high temperatures [13-16]. Therefore, it is necessary to characterise and compare the mechanical properties of this material using different testing approaches. In this way, well-designed experiments coupled with reliability analysis can optimise rational designs that ensure the successful use of ceramics in demanding structural applications[17]. The purpose of this paper is to compare the fracture strength of BSCF obtained from both uniaxial and biaxial bending tests and evaluate both tests by means of Weibull statistics. Fracture analysis is also performed in order to determine and characterise the failure origins.

2 Theory and governing equations

Because uniaxial and biaxial bending tests represent different stress states and different test volumes or surface areas, Weibull analysis is used to study this difference and determine whether it is simply an effect of loading geometry. The simplest treatment of the size dependence of strength is through the application of Weibull statistics based on the fracture theory[18]. Assuming the two-parameter Weibull distribution, the probability (F) of failure of a component is given by[19, 20]

$$F = 1 - \exp\left[-\left(\frac{\sigma_{\max}}{\sigma_c}\right)^m V_{\text{eff}}\right] \quad (1)$$

where $\sigma_{\max}$ is reference maximum stress in the stressed solid, m Weibull modulus, σ_c characteristic strength, and V_{eff} effective stress volume defined by

$$V_{\text{eff}} = \int \left(\frac{\sigma}{\sigma_{\max}}\right)^m dV \quad (2)$$

where σ is the local stress in an elemental stressed volume d_v . Equation (1) can be simplified as follows:

$$\ln\left(\frac{1}{1-F}\right) = \left(\frac{\sigma_{\max}}{\sigma_c^*}\right)^m \quad (3)$$

where the parameter σ_c^* [$\sigma_c^* = \sigma_c(V_{\text{eff}})^{\frac{1}{m}}$] represents the specific characteristic strength of the specimen at $F=0.632$; and F , the failure probability, is defined by the relation[21]:

$$F = (i - 0.5)/N \quad (4)$$

where i is the ranking number of a specimen in sample size N in increasing order of fracture stress σ . To analyse fracture strength data, Equation (3) can be rewritten as follows[21]:

$$\ln\ln\left(\frac{1}{1-F}\right) = m\ln\sigma_{\max} - m\ln\sigma_c^* \quad (5)$$

Hence, a plot of the left side of Equation (3) as a function of the natural logarithm of fracture stress should obtain a straight line with a slope of m .

Average strengths in uniaxial and biaxial bending tests are related to the effective volumes by the relation[22]:

$$\frac{\sigma_{3P}}{\sigma_{\text{ROR}}} = \left(\frac{V_{\text{ROR}}}{V_{3P}}\right)^{\frac{1}{m}} \quad (6)$$

The effective volume for the ring-on-ring test (ROR) has been given by Batdorf[23] and Breder[18]:

$$V_{\text{ROR}} = 2t\pi r_i^2 m^{0.45} \quad (7)$$

where r_i is the radius of the loading ring. The effective volume for the three-point bending test (3P) is given by [24]:

$$V_{3P} = \frac{Lhb}{2(m+1)^2} \quad (8)$$

L is the distance between the two support points, b is the width of the cross section at the applied load, and h is the thickness of the specimen. The effective volume is regarded as an assumed volume where the tensile stress is applied. Combining Equations (6), (7) and (8), the fracture strength obtained by either test method can be used to predict the fracture strength measured by the other.

3 Experimental procedure

3.1 Sample preparation

Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} powder was supplied by Treibacher Industrie AG, Austria. The powder was packed in a cylindrical stainless steel die with a diameter 28 mm, and uniaxially pressed under a pressure of 100 MPa. The as-pressed BSCF powder was then sintering at a temperature of 1100 °C for 10 hours. The heating rate and the cooling rate during the process of sintering were set to 180 °C/hour. After sintering, the diameters of the specimens shrank from 28 mm to approximately 22 mm. The as-sintered BSCF bulk were cut into disc-shaped and bar-shaped specimens using a diamond cutting blade in a precision cut-off machine (Accutom 5, Struers). The specimens were ground with SiC paper with different grit sizes from P400 to P1200, and then polished with diamond paste descending from 6 μm to the final stage of 1 μm. The disc-shaped specimens for the ring-on-ring tests had a diameter of ~ 22 mm, and thickness of ~ 1 mm. The bar-shaped specimens for the three-point bending tests

had a dimension of $\sim 2.1 \times 2.3 \times 14 \text{ mm}^3$. All the surfaces were ground and polished before any mechanical testing.

3.2 Mechanical testing procedure

Mechanical testes were carried out using biaxial and uniaxial bending tests on an Instron 5569 test machine at both RT and 800 °C in air. The load was applied within an accuracy of 0.01 N and the displacement was recorded within an accuracy of 0.001 mm. Thermocouples near the test specimens were used to monitor the temperatures of the specimens at 800 °C. 10 specimens were used for each method at RT and 800 °C, respectively. The force was applied at a rate of 100 N/min by a computer-driven load cell and a sensor was used to record the applied load and the displacement of the specimen. The peak load was used to calculate the fracture strength. Prior to the test, the testing fixtures (made of alumina) were aligned with respect to the loading nose (made of alumina) to ensure that the loading was symmetrical. For the tests at 800 °C, a heating rate and a cooling rate of 180 °C/hour were used, and a dwell time of 1 hour was chosen to reach a uniform temperature all over the sample before testing.

The ring-on-ring bending test was conducted as a type of biaxial bending tests in this work. The schematic picture of the test is shown in Figure 1:

The test conditions were in accordance with the ASTM standard C1499-05[25]. The fracture strength was calculated using the following equation:

$$\sigma_f = \frac{3P}{2\pi t_h^2} \left[(1 + \nu) \ln \left(\frac{r_2}{r_1} \right) + \frac{1-\nu}{2} \left(\frac{r_2^2 - r_1^2}{r_3^2} \right) \right] \quad (10)$$

where P is the peak load, t_h is the specimen thickness, ν is the Poisson ratio. r_1, r_2 , and r_3 are the radii of the loading ring, the supporting ring and the specimen, respectively. The values of t_h , r_1 , r_2 and r_3 are 1.0, 1.9, 8.4, 21.8 mm, respectively. Poisson ratio is taken as 0.3. The three-point bending test was conducted as a type of uniaxial bending tests to measure the fracture strength of BSCF in this work. The schematic diagram of the three-point bending test is shown in Figure 2. The calculation of the fracture strength was performed based on ASTM Standard C 1161[26] using the following equation:.

$$\sigma_f = \frac{3PL}{2bh^2} \quad (11)$$

where P is the peak load, L is the distance between the two support points, b is the width of the cross section at the applied load, and h is the thickness of the specimen. The mean values of b, h, L are 2.1, 2.3, and 8 mm, respectively.

3.3 Microstructural characterisation

The relative densities of all the BSCF specimens determined by the Archimedes method in distilled water were over 94%. The phase composition of all the BSCF was determined to be a single cubic phase by X-ray diffraction. The diameter of grain size was determined to be 22 μm using the area counting technique. Details of these compositional and microstructural features can be found elsewhere[27]. The fracture surface were analysed based on the fractographic principles[28]. The pore size was quantified by Image-Pro Plus 6.0 software based on SEM images.

4 Results

4.1 Fracture strengths and Weibull analysis

Biaxial and uniaxial fracture strengths were measured using ring-on-ring and three-point bending tests at both RT and 800 °C, respectively. The results are summarised in Table 1 which gives the specimen number (N), the mean fracture strengths and corresponding standard deviations, the coefficients of variation, the characteristic strength (σ_c), the Weibull modulus (m) and standard errors, coefficients of correlation (R^2).

Figure 3 shows Weibull plots of fracture strengths evaluated by both methods at RT and 800 °C. The Weibull modulus m and characteristic strength σ_c are determined from the slope and the intercept of the straight line fitted by linear regression, respectively, and summarised in Table 1. The biaxial strength data give $m=10.2$ ($R^2 = 0.91$) at RT and $m=5.5$ ($R^2 = 0.95$) at 800 °C, while the corresponding values for the uniaxial strength at RT and 800 °C are 9.6 ($R^2 = 0.94$) and 5.4 ($R^2 = 0.91$), respectively. The Weibull modulus obtained from the biaxial bending tests is similar to that obtained from the uniaxial bending tests at both RT and 800 °C, respectively. It suggests that there is little difference in the flaw population between these two experiments and the effective volume calculations are valid for the both room and high temperatures.

It is noted that the fracture strengths here are lower than those obtained from Huang *et*

al.[10] who have studied the strengths of BSCF between RT and 800 °C using the ring-on-ring bending test. Compared with the BSCF specimens studied in this work, the specimens used by Huang *et al.*[10] show similar porosity, but smaller grain sizes. Therefore, one possible explanation of the difference is that the defect size, which is critical to determining the fracture strength, can be related to the grain size. Another possible reason is a larger effective volume for this present experiment, which leads to smaller fracture strength according to Equation (6), although the same method is used to determine the fracture strength.

For all the specimens evaluated in this work at both RT and 800 °C, as seen in Table 1, the fracture strengths obtained by the uniaxial tests are significantly higher than those determined by the biaxial tests. This finding is consistent with the study by Shetty *et al.* [22] who have also found the strengths of alumina determined by the uniaxial bending test were higher than those obtained by the biaxial method. The discrepancy is attributed to the difference in the effective area or volume of the material subjected to maximum stress between these two tests [18]. To be more specific, by accounting for the effective volume of the materials under stress [Equations (8) and (9)] it is found that biaxial specimens ($V_{\text{eff}}=20.5 \text{ mm}^3$) are subjected to a larger effective volume than that of the three-point bending specimens ($V_{\text{eff}}=0.17 \text{ mm}^3$), which then results in a smaller fracture strength obtained by the biaxial test according to Equation (6).

The fracture strength measured by either test can be predicted by that measured by the

other using Equations (6), (7) and (8). For example, the predicted fracture strengths of the three-point bending tests are plotted in Figure 4 based on the measured fracture strengths by the ring-on-ring bending tests. The predicted strengths of the three-point bending test based on the ring-on-ring tests are only 6.3% and 10.3% lower than the measured strengths from the three-point bending tests at RT and 800 °C, respectively, as shown in Table 2. The ratios of fracture strengths measured by these two methods are also similar to those obtained from the predictions at both RT and 800 °C. This comparison suggests that the predicted approach is adequate for the present case.

For all the specimens evaluated in Table 1, it should be noted that the coefficient of variation obtained at 800 °C is twice higher than those at RT as for both tests, which may be caused by the change of defects size during heating due to the thermal expansion and the randomness of the mechanical properties at high temperature[29]. The coefficients of variation determined by the biaxial bending tests at RT and 800 °C are less than those determined by the uniaxial bending tests (Table 1). However, the standard deviations determined by the biaxial bending tests at RT and 800 °C are slightly higher, which may be attributed to the complex stress state developed and the frictional force between the contact surface[29].

Figure 5 shows the typical load-displacement curves of different testing methods at both RT and 800 °C. In the case of the same method, the failure deflection of the specimen at 800 °C is larger than that at RT. On the other hand, the load-deflection curves obtained from these two methods at RT are linear while the curves obtained at

800 °C are nonlinear. This indicates that the plastic deformation of the BSCF specimens (e.g creep) occurs at 800 °C. The nonlinear load-deflection curve was also observed in $\text{LaCrO}_{3-\delta}$ and was attributed to the formation of oxygen vacancies at high temperature[30]. Previous studies [31, 32] have also shown that BSCF materials release oxygen and form oxygen vacancies at high temperature. However, according to the load-deflection curves at 800 °C, the slopes of the curves increase with increasing deflection, suggesting an increase in deformation resistance of the material. This change could not be caused by the formation of vacancies as it would lead to a decrease in material strength. A more plausible explanation is pore closure induced by compressive stress at 800 °C, which makes the further deformation more difficult. Compared with the three-point bending tests, the deflections in ring-on-ring bending tests are larger at both RT and 800 °C due to their larger effective volume.

4.2 Fractography

It is important to study the fracture surface, fractography, which can shed light on not only the process of fracture but also failure origins. In general, fracture surfaces are often observed as transgranular or intergranular. After the ring-on-ring and three-point bending tests, the fracture surfaces of BSCF tested at RT and 800 °C are investigated by the SEM to determine the fracture modes, and the morphology of the fracture surfaces is shown in Figure 6. At both RT and 800 °C the BSCF specimens show the transgranular mode, similar to previous studies reported in the literature[10]. As shown in Figure 6(B), additional particles are observed along the grain boundaries

and in the inner part of the grains after high temperature testing. However, the XRD investigation does not give any indication with respect to the presence of other phases, probably due to the fact that the amount of these particles is too low and therefore beyond the detecting capability. The only detectable phase on the fracture surface from all the specimens is cubic BSCF. Efforts have been made to determine the compositions of the small particles using EDS. However, no difference in compositions has been found between the matrix phase and these particles. Additional work is required to unequivocally determine the composition and structure of these small particles by transmission electron microscopy in future. However, examination on the BSCF surface prepared by grinding and polishing shows no such particles (Figure 6(C)). This indicates that the particles only exist at the surface, possibly formed through the reaction between the crack surface and carbon dioxide in the air at high temperature after failure[33]. Therefore, these particles should have no influence on the measured fracture strength of BSCF at 800 °C.

5 Discussion

For these two bending methods, both fracture strengths and Weibull modulus obtained at 800 °C are respectively lower than those obtained at RT. It has been reported by Rutkowski *et al.*[13] that the interatomic distance increases due to chemical expansion associated with oxygen release at 800 °C, which should result in decreasing strength. The lower Weibull modulus indicates a significantly larger scattering of fracture strengths at 800 °C. It is probably caused by the increase of the defect size during

heating due to the thermal expansion and the randomness of mechanical properties at high temperature, which results in a different flaw size distribution between RT and 800 °C.

In order to understand the failure mechanism of BSCF upon loading, the failure origins need to be determined. As mentioned above, there is little difference in flaw distribution between three-point and ring-on-ring bending tests. In addition, compared with the examination of fracture surfaces obtained from ring-on-ring bending tests, the failure origins of the specimens broken by three-point bending tests are much more convenient to be examined. Therefore, the focus here is to find and study the failure origins of the specimens fractured by the three-point bending tests

For each case, fracture positions always initiate on or near the tensile side of the specimens. The large pores shown in Figure 7, near the tensile face, are regarded as failure origins as the pores can act as stress concentrators and lead to the failure of the specimens. This is further confirmed by the fact that the regions surrounding the fracture origins are smoother than the remainder of the surface and fracture lines emanate from the large pore as shown in Figure 7 (A). Other characteristic failure origins include edge fracture and surface cracks.

Figure 8 shows the character of the failure origin of each specimen loaded by the three-point bending tests at RT and 800 °C. Fractography analysis was performed on the fracture surface of BSCF and the type of the failure origin is indicated by an arrow in Figure 7. A capital letter with an arrow refers to the character of a fracture origin; P,

E and C correspond to a pore, edge fracture and surface crack.

The fracture origins of most BSCF specimens at both temperatures were porous regions extending 40–80 μm , as exemplified from the selected fractography in Figure 7. This size is larger than the maximum defect size (56 μm) measured on the specimen surface, as shown in Figure 9(A). In addition, the pore size distributions of the specimens having the maximum and minimum fracture strength are similar, as shown in Figure 9(B). The maximum defect size (56 μm) measured is lower than the maximum pore size at the fracture origin observed on the fracture surface ($\sim 80 \mu\text{m}$). This disagreement can be ascribed to a relatively small area (1 mm^2) utilised for counting defects. According to the model proposed by Quinn[24], the effective surface area of a flexural BSCF specimen by the three-point bending test at RT in this study is calculated to be 3.62 mm^2 with a Weibull modulus of 9.6. Therefore, it is necessary to enlarge the examination area for counting defects in order to discover those critical contributions to the fracture of flexural specimens. To achieve this, the defect frequency data are extrapolated to the larger defect size region to estimate the maximum defect size possibly existing in the flexural specimens. The number of defects at a given size was recalculated per 1 mm^2 . Note that the number of defect sizes also depends on the range for counting and is normalised by dividing it by the employed counting range, 1 μm [34]. The result is shown in Figure 9(C). The defect frequency corresponding to the flexural specimen is determined to be 0.31, statistically (One defect for the effective surface areas; $1/3.62=0.28$), and the resultant defect size is 80 μm . This gives a relatively acceptable defect size, although more

detailed observations are needed for this defect frequency.

It should be noted that the fracture strength can be also determined from the relationship between the critical defect and the fracture toughness, according to the following equation:

$$\sigma_f = \frac{K_{IC}}{Y\sqrt{c}} \quad (12)$$

σ_f is the fracture strength; K_{IC} is the fracture toughness; Y is the flaw shape factor; c is the critical flaw size. According to the guidance of fractographic investigation[28], Y value of the bulk failure origin is 1.47. It has been also reported that the fracture toughness of BSCF at RT is approximately 1 MPa·m^{0.5} [35]. The fracture strength of the BSCF (81MPa) specimen shown in Figure 7(A) is similar to that (87MPa) estimated from the Equation (12).

6 Conclusion

The present study evaluates the fracture strengths and the Weibull modulus of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) materials by means of biaxial and uniaxial bending tests at RT and 800 °C. The fracture strengths obtained from biaxial bending tests at RT (73 MPa) and 800 °C (45 MPa) were lower than those obtained from uniaxial bending tests at RT (127 MPa) and 800 °C (107 MPa), respectively, because the effective volume of the former testing method is larger than the latter. The Weibull modulus obtained from the biaxial tests were similar as those obtained from the

uniaxial tests at RT and 800 °C, respectively. It suggests that there is little difference in the flaw population between these two experiments. However, the Weibull modulus obtained at 800 °C was much lower than that obtained at RT. It is probably caused by the change of defects size during heating due to the thermal expansion and the randomness of mechanical property at high temperature, which results in a different flaw size distribution between RT and 800 °C. Fracture surfaces at both RT and 800 °C show only a transgranular mode. Most defects in this particular material are found to large pores, suggesting that the use of BSCF for membrane applications requires careful control of the sintering process in order to eliminate the pore coalescence or cavities.

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Figure 1 Schematic illustration of the ring-on-ring bending test: (A) overview; (B) cross-section

Figure 2 Schematic illustration of the three-point bending test

Figure 3 Weibull plots of the fracture strengths of BSCF evaluated at RT and 800 °C: (A) ring-on-ring bending tests; (B) three-point bending tests

Figure 4 Strength distributions measured by experiments and three-point bending strengths predicted from the ring-on ring bending tests at: (A) RT; (B) 800 °C.

Figure 5 Typical load-displacement curves of different testing methods at RT and 800 °C

Figure 6 Typical fracture surfaces of BSCF at: (A) RT; (B) 800 °C. Numerous small particles are observed on the fracture surface of the BSCF specimen tested at 800 °C. (C) Surface prepared by grinding and polishing after testing at 800 °C, showing no particles inside the grains or along the grain boundaries.

Figure 7 Fracture origins found on the BSCF specimens after three-point bending tests at (A) RT and (C) 800 °C. (B) and (D) show the high-magnification images of (A) and (C), respectively.

Figure 8 Character of the failure origin of each specimen carried out by three-point bending tests at RT and 800 °C

Figure 9 (A) Typical low-magnification SEM micrograph of BSCF sintered at 1100 °C for 10 hours; (B) Histogram of the pore size distributions of BSCF specimens with the highest and lowest fracture strength; (C) Defect size estimated for a large area using the measured data. The red arrow indicates the estimated largest defect size corresponding to the effective surface area of the BSCF sample

Table 1 Results of uniaxial and biaxial bending tests at RT and 800 °C

Method	Temperature	Specimen number(N)	Mean fracture strength σ_f (MPa)	Standard deviation (MPa)	Coefficient of variation (%)	Weibull modulus (m)	Standard error	Characteristic strength(σ_c)	Coefficients of correlation(R^2)
Uniaxial test	RT	10	127	15	11.8	9.6	0.7	133	0.95
	800 °C	10	107	24	22.4	5.4	0.3	116	0.96
Biaxial test	RT	10	73	7	9.6	10.2	1.3	77	0.91
	800 °C	10	45	9	20	5.5	0.4	48	0.95

Table 2 Results of measured values of two methods and the predicted values of three-point bending tests

Temperature	Measured		Predicted	Ratio	
	σ_{3p} (MPa)	σ_{bia} (MPa)	σ_{3p} (MPa)	σ_{3p}/σ_{bia}	$\sigma_{3p}(\text{predicted})/\sigma_{bia}$
RT	127	73	119	1.74	1.63
800 °C	107	45	96	2.38	2.18