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Subcritical crack growth behaviour of a perovskite-structured $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ oxygen transport membrane

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Abstract

This paper herein studies subcritical crack growth (SCG) behaviour of a perovskite-structured $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) as an oxygen transport membrane material. The SCG behaviour of BSCF is evaluated by a constant load method and constant stress rate method at room temperature (RT) and 800 °C in air, respectively. The low crack velocity measurements are carried out by ring-on-ring bending tests while the high crack velocity measurements by compact tension tests. The stress rates vary approximately from 0.1012 to 101.2 MPa/min. The fracture stress increases with increasing stress rate at 800 °C. The SCG parameter, n , of BSCF is determined to be 24.32 and 13.83 at RT and 800°C in air, respectively. This indicates that BSCF is more susceptible to SCG at 800°C. The strength-probability-time (SPT) diagram is constructed for design proposes. The stress for a lifetime of 40 years should not exceed 27.21 MPa at RT or 4.53 MPa at 800 °C to assure a failure probability below 1%.

Keywords: BSCF; Subcritical crack growth; SPT diagram; stress rate; lifetime

1 Introduction

Currently, mixed ion-electron conducting (MIEC) materials have been attracting great attention due to their high oxygen permeations, which makes them promising materials for oxygen separation membrane applications [1-4]. Among these MIEC materials, the perovskite-structured $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) has been of great interest due to its 100% selective permeation in theory and high-efficiency properties at elevated temperatures during the operation process[5]. In real applications, these MIEC membranes are challenged not only by the high operating temperature ($\sim 800\text{ }^{\circ}\text{C}$), but also the high oxygen pressure gradient through the membrane and chemically induced strains which is attributed to the decrease in the chemical expansion at high temperature[6]. Besides the high oxygen permeability concerned [7, 8], the MIEC membranes also need to maintain their geometrical and structural integrity, because they are subjected to complex mechanical stresses and stress cycles during service. Therefore, mechanical properties need to be assessed.

So far, most of the available literature on the mechanical properties of BSCF has focused on its fracture strength[9-11], Young's modulus[12, 13], fracture toughness [10, 14] and hardness as well as how these properties are correlated to microstructure and composition[15]. In addition, creep studies of BSCF also provide important information on its mechanical properties at high temperatures [16-18]. Under

operating conditions, another important mechanical property, subcritical crack growth, also needs to be investigated. In fact, the long-term performance of a ceramic component is not only determined by the initial strength and fracture toughness, but also depends on its SCG resistance. For ceramics sensitive to SCG, the strength of the components in service usually decreases with increasing service time. Studying SCG can predict material lifetime and is helpful to structural design of brittle materials. With regard to lifetime predictions in particular, the lowest crack growth rates are the most important to lifetime predictions and therefore it is of considerable interest to acquire information about very slow crack growth rates down to 10^{-12} m/s [19]. For a ceramic under conditions of SCG, a finite lifetime has to be expected. It has been demonstrated that the dense BSCF are more sensitive to SCG than the porous ones at ambient air, which is probably attributed to crack tip blunting by pores [11]. Although the SCG of BSCF at RT has been evaluated by a constant stress rate method [6, 11], there is no literature on its SCG at high temperatures to our best knowledge. It is clear that a more general approach to the characterisation of the mechanical behaviours is required. In this way, well-designed experiments coupled with reliability analysis can optimise rational design decisions that ensure the successful use of ceramics in demanding structural applications [20]. The purpose of this work is to determine the SCG parameters of BSCF at RT and 800 °C using a constant load method and constant stress rate method, respectively. The strength-probability-time diagrams at RT and 800 °C are also plotted for design purposes. The fracture surfaces are analysed by X-ray diffraction (XRD) and scanning electron microscope (SEM) to explain the

changes in mechanical properties and reliability.

2 Experimental procedures

2.1 Sample preparation

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ powder was supplied by Treibacher Industrie AG, Austria. The powder was packed in a cylindrical stainless-steel die with a diameter of 28 mm, and uniaxially pressed under a pressure of 100 MPa. The pellets were then transferred to a Carbolite box furnace and sintered at 1100 °C for 10 hours. The heating and cooling rate during the process of sintering were set to 180 °C/hour. After sintering, the diameters of the pellets shrank from 28 mm to approximately 22 mm. The sintered pellets were cut into disc-shaped (ϕ 22 mm $\times$ 1 mm) and rectangular plate (12.5 $\times$ 12 $\times$ 2 mm³) specimens for the ring-on-ring and compact tension tests, respectively, 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 μ m to a final stage of 1 μ m.

2.2 Determination of fracture toughness and fracture stress at RT and 800°C

The indentation strength method was applied to determine the fracture toughness of BSCF at RT and 800°C. The fracture toughness is given by [21]

$$K_{IC} = 0.59 \left(\frac{E}{H} \right)^{\frac{1}{8}} [\sigma_f P^{\frac{1}{3}}]^{\frac{3}{4}} \quad (1)$$

where E Young's modulus(MPa); H hardness(MPa); σ_f fracture stress(MPa); P indentation load(N)

The fracture stress was determined by the ring-on-ring bending test[22]. The test conditions were in accordance with the ASTM standard C1499-05[23]. The fracture stress was calculated using the following equation:

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

where P was the peak load, t_h was the specimen thickness, ν was the Poisson ratio. r_1, r_2 , and r_3 were the radii of the loading ring (1.0 mm), the supporting ring (1.9 mm), and the specimen (21.8 mm), respectively. Poisson ratio of BSCF was taken as 0.3 from the reference [11].

Five disc-shaped samples were used to determine the fracture toughness of BSCF by the indentation strength method using ring-on-ring bending tests at both RT and 800 °C. These specimens were indented by a micro-hardness tester with a load of 10 N prior to bending. In order to eliminate the effect of the indentation related residual stress on the subsequent crack propagation during the ring-on-ring tests, the samples were annealed after indentation at 800 °C for 30 mins.

2.3 Constant load method at RT

The ring-on-ring bending test was carried out to determine the low crack growth rate

(<10⁻⁷ m/s) while the compact tension test was used to determine the high crack growth rate (>10⁻⁷ m/s).

The SCG rate was characterised by the dependence of the crack velocity, v , on the mode I stress intensity factor K , and can be expressed by the empirical power relationship[24]:

$$\log(v) = n \log\left(\frac{K}{K_c}\right) + \log(A_0) \quad (3)$$

where A_0 and n are constants for a given material, and K_c is the critical stress intensity factor or the fracture toughness determined by indentation strength method using Equation (3). The average crack growth rate was given by:

$$v = \frac{\Delta c}{\Delta t} \quad (4)$$

where Δc is the increased crack length before and after the experiment and Δt the elapsed time

2.3.1 Low crack growth rate measurement

The ring-on-ring bending test was used to investigate the low crack growth rate of BSCF. The stress intensity factor K is determined by the equation as follows [24]:

$$K = Y\sigma\sqrt{c} \quad (5)$$

the stress can be obtained from the Equation (2); Y is related to crack shape.

Indentation impressions were introduced onto the BSCF specimen surfaces using an instrumental microindentation with a maximum load of 10N. In order to eliminate the residual stress around the indented areas, the samples were annealed at 800 °C for 30 mins. The specimens were subjected to different static loads under a prescribed duration, Δt , during the ring-on-ring bending tests. The maximum length of time is 14 days for the test procedure. The crack length was measured via SEM after unloading, with a precision of $\pm 0.1 \mu\text{m}$, and v is defined as the ratio of the crack increment, Δc (the crack length from c_1 to c_2), to the loading time, Δt (the time from t_1 to t_2):

$$v = \frac{c_2 - c_1}{t_2 - t_1} \quad (6)$$

The corresponding average stress intensity factor can be determined as follows:

$$K = \frac{\int_{t_1}^{t_2} Y \sigma \sqrt{c} dt}{t_2 - t_1} \quad (7)$$

2.3.2 High crack growth rate measurement

The compact tension test was used to investigate the high crack growth rate of BSCF. With regard to preparation of the compact tension (CT) sample, two holes were drilled to fix the sample. A precrack was created by cutting a half chevron notch from the center of one side, which has been described by Meschke *et al.*[25]. The tip of the notch was typically 1.5 mm wide. The stress intensity factor K_I is given by[26]

$$K_I = \frac{P}{B} \sqrt{\frac{\pi}{W}} \left[16.7 \left(\frac{c}{W} \right)^{0.5} - 104.7 \left(\frac{c}{W} \right)^{1.5} + 369.9 \left(\frac{c}{W} \right)^{2.5} - 573.8 \left(\frac{c}{W} \right)^{3.5} + 360.5 \left(\frac{c}{W} \right)^{4.5} \right] \quad (8)$$

where P is the applied load; B is the thickness of the specimen ($\sim 2\text{mm}$); c is the crack length ($\sim 3.5\text{ mm}$); and W is the width of the specimen ($\sim 10\text{mm}$).

In order to eliminate residual stress introduced during mechanical cutting, the specimens were annealed at $800\text{ }^{\circ}\text{C}$ for 30 mins. The crack length was measured via SEM after unloading, with a precision of $\pm 0.1\text{ }\mu\text{m}$. The corresponding stress intensity factor K can be determined as an arithmetic mean value between two consecutive crack length measurements made while the crack was growing under a constant load.

2.4 Constant stress rate at $800\text{ }^{\circ}\text{C}$

The ring-on-ring bending test was used to investigate the slow crack growth at $800\text{ }^{\circ}\text{C}$ in air. Four different loading rates, 0.1 N/min , 1 N/min , 10 N/min , and 100 N/min , were used, corresponding to the stress rates of 0.1012 MPa/min , 1.012 MPa/min , 10.12 MPa/min and 101.2 MPa/min . Five specimens were tested at each loading rate at $800\text{ }^{\circ}\text{C}$ in air. Each specimen was held at $800\text{ }^{\circ}\text{C}$ for 1 hour before testing. The heating and cooling rates were set to be $180\text{ }^{\circ}\text{C/h}$.

The SCG effect can be assessed in a test with constant stress rate $\dot{\sigma}$, where the fracture stress σ_f is correlated with the stress rate using the equation[27]:

$$\log \sigma_f = \frac{1}{n+1} \log \dot{\sigma} + \log D \quad (9)$$

where n and D (Pa/s) are the SCG parameters. The stress rate is calculated from[23]

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

where $\dot{P}$ is the load rate (N/min), other parameters have the same meaning as in Equation 2.

2.5 Microscopy observation and X-ray diffraction analysis

The phases present in all the BSCF specimens were determined by X-ray diffraction (XRD; PW1830, Philip, Eindhoven, the Netherlands) with Cu K_{α} radiation ($\lambda=1.54060$ Å) operating at 40 kV/40 mA. Microstructural investigations of the specimens were carried out by scanning electron microscope (SEM, Quanta 650). The crack lengths were measured based on a series of high-resolution SEM images. The SEM images were acquired under a backscattered electron (BSE) imaging mode, which gives a great contrast between the crack and bulk material. Image J software was then used to extract the profiles of the cracks based on the contrast of the SEM images. The error of these measurements is estimated to be within a few pixels, which is approximately 0.1 μm . The chemical composition was determined by energy-dispersive X-ray spectroscopy (EDS) equipped on a SEM (FEI, Quanta 650). In order to observe crack path below the surface, a focused ion beam (FIB, Quanta 3D, FEI) was used to cut through the crack to reveal the subsurface microstructure.

3 Results

3.1 Determination of fracture toughness at RT and 800°C

The fracture toughness determined by ring-on-ring bending tests were 1.12 ± 0.07 MPa·m^{0.5} and 0.81 ± 0.08 MPa·m^{0.5} at RT and 800°C according to the Equation (1), respectively. Both values were similar to those obtained by other groups [14, 15]. According to the research conducted by Chantikul *et.al*[28], the uncertainties in E/H are relatively unimportant. Indeed, since this ratio varies only between 10 and 50 for most ceramics, replacement of $0.59(\frac{E}{H})^{0.125}$ by an averaged quantity would add no more than 10% to the error of K_{IC} for a material whose elastic/plastic parameters are totally unknown[28]. Additionally, the differences between the values of fracture toughness from the indentation strength and the standard indentation method was less than 5% at room temperature [15]. In other words, these two methods are in good agreement with each other for BSCF. The typical fracture origins of all the samples were the indentation-induced cracks as shown in Figure 1. It revealed a fracture surface in a semi-circular zone directly underneath the impression (red dotted line) where compressive stresses predominated during the indentation process.

3.2 Determination of SCG parameters at RT

Figure 2 shows the evolution of a crack tip during a period of dwell time of 3600 seconds under a constant load of 50 N in a ring-on-ring test. Comparison of the images clearly shows that the crack tip propagated 6.0 μm at a stress intensity factor

of $0.68 \text{ MPa}\cdot\text{m}^{0.5}$ during 1 hour, and the crack growth rate was calculated to be $1.67\times 10^{-9} \text{ m/s}$.

The results obtained by the ring-on-ring bending tests and compact tension tests are represented in Figure 3. Above a stress intensity factor of $0.75 \text{ MPa}\cdot\text{m}^{0.5}$, high crack growth rates over 10^{-7} m/s were determined by compact tension tests. When the applied stress intensity factors of K_I are between 0.55 and $0.75 \text{ MPa}\cdot\text{m}^{0.5}$, a detailed measurement over a wide range of crack velocities has been conducted. Further reduction of the applied stress intensity factor down to $0.54 \text{ MPa}\cdot\text{m}^{0.5}$ led to no crack propagation even after two weeks. As mentioned previously, the maximum length of time is 14 days for a test procedure, so the threshold values are proposed based on the assumption that crack velocities higher than $10^{-13}\sim 10^{-14} \text{ m/s}$ are detectable with the experimental procedure used. Nevertheless, further crack propagation might take place after sufficiently long time but lies below the detection limit of the method used. For most oxide ceramics, it is believed that [29, 30] stress corrosion by water at the crack tip is the mechanism that is responsible for crack propagation at room temperature when the stress intensity factor is below the fracture toughness. The SCG value, n , is known as the fatigue susceptibility parameter. The linear fitting in the $\log(K_I/K_{IC})-\log(v)$ representation between 10^{-7} and 10^{-10} m/s finally yields $n=24.32\pm 2.1$ with a $R^2=0.908$, which reasonably agrees with that determined by the constant stress rate method at RT by Pećanac *et al.* [11].

The scatter of the data of the crack growth rate is due to crack blunting and crack

branching caused by microstructural defects (e.g. pores), which can induce an decrease in the crack tip stress intensity factor[31, 32] and will be discussed below.

When a crack meets a pore in a ceramic material, the crack tip blunts[31]. An example of this crack blunting is given in Figure 4. This decreases the stress intensity at the crack tip and requires an increase of the external load to propagate the crack. Therefore, the pores are regards as barriers for crack growth. However, it should be noted that as the pore fraction of the BSCF used in this work is small and the crack areas in contact with pores are limited, the effect of pores on crack blunting is expected to be minor.

Apart from crack blunting, crack branching (Figure 5) was also observed on the surface when a main crack propagates. It has been reported that crack branching can be the result of many interacting microcracks or microbranches[32]. To be more specific, when a crack propagates in a material containing a great number of pores, the crack passes through these pores and some pores can change the crack growth plane[33]. In addition, crack branching also can be caused by the microcracks that are entirely embedded in the interior of the bulk[32]. Figure 6 shows a cross-section of a crack cut through the surface using a FIB. It is clearly shown that crack branching occurred in the interior of the bulk.

3.3 Determination of SCG parameters at 800°C

The SCG parameters n and D in Equation (9) can be obtained by fitting log (fracture

stress) against log (stress rates) using a linear regression analysis. The slope of the linear regression line, α , is determined by the following equation [27]:

$$\alpha = \frac{K \sum_{j=1}^K (\log \dot{\sigma}_j \log \sigma_j) - (\sum_{j=1}^K \log \dot{\sigma}_j \sum_{j=1}^K \log \sigma_j)}{K \sum_{j=1}^K (\log \dot{\sigma}_j)^2 - (\sum_{j=1}^K \log \dot{\sigma}_j)^2} \quad (11)$$

where K is the sample size, $\dot{\sigma}_j$ is stress rate and σ_j is the fracture stress. The SCG parameter n is determined as $n = (1/\alpha) - 1$.

The intercept, β , of the linear regression line is determined by the following equation [27]:

$$\beta = \frac{(\sum_{j=1}^K \log \sigma_j) \sum_{j=1}^K (\log \dot{\sigma}_j)^2 - (\sum_{j=1}^K (\log \dot{\sigma}_j \log \sigma_j)) (\sum_{j=1}^K \log \sigma_j)}{K \sum_{j=1}^K (\log \dot{\sigma}_j)^2 - (\sum_{j=1}^K \log \dot{\sigma}_j)^2} \quad (12)$$

the SCG parameter D is determined by $D = 10^\beta$.

The plot of Equation (9), log (fracture stress) vs log (stress rate), is shown in Figure 7.

The SCG parameters n and D are determined as 13.83 ± 0.97 and 30.34 ± 1.15 at 800°C , respectively.

3.4 Stress-probability-time (SPT) diagrams

Considering the design in application, it is essential to predicting the lifetime of the ceramic membranes. Therefore, it is desirable to construct a SPT diagram of BSCF which describes the failure probability as a function of stress and time. To set up SPT diagrams, the stress is changed to an equivalent stress, σ_{1s} , which denotes that the

stress transforms the failure stress σ_f tested at a stress rate $\dot{\sigma}$ into an equivalent stress that would result in the failure of the sample in 1 second[34] using the following equation:

$$\sigma_{1s} = \sigma_f \left(\frac{\sigma_f}{\dot{\sigma}(n+1)} \right)^{1/n} \quad (13)$$

where n is the SCG parameter.

(1) SPT at room temperature

The characteristic strength (σ_0) and Weibull modulus (m) of the ring-on-ring bending samples have been reported to be 77 MPa and 10.2 at RT, respectively, in our previous work[22]. The corresponding stress rate is 101.2MPa/min. The basic processes of constructing SPT diagrams for the samples are given as follows:

- (i) Using the SCG parameter $n=24.32$ and $\sigma_0 = 77$ MPa in Equation (13), the equivalent stress that would result in the failure of the sample in 1 second is 78.42MPa.
- (ii) Combination of this stress and $1-F=1/e$ (corresponding to the characteristic strength σ_0 ; e is Euler's constant), where F is failure probability, shows the first data point of the 1 second line on the SPT diagram.
- (iii) Plot the 1 second line with a slope of Weibull modulus 10.2.
- (iv) A series of lines parallel to the 1 second line, with spacing between the lines equalling to $(\ln 10)/n$ or $2.3/n$. The spacing $2.3/n$ represents a change in

life-time by a factor of 10[35]. Each line represents a decade increase in lifetime.

Some selected prediction lines are shown in Figure 8

On the basis of the SPT diagram in Figure 8, the stress for a tolerable failure probability can be predictable; for example the stress for a lifetime of 40 years should not exceed 27.21 ± 1.74 MPa to assure a failure probability below 1% at RT. This implies that the applied stress which imposes on the membranes should not be beyond this value at RT.

(2) SPT at 800°C

The characteristic strength (σ_0) and Weibull modulus (m) of the ring-on-ring bending samples have been reported to be 48 MPa and 5.5 at 800 °C, respectively, in our previous work[22]. The corresponding stress rate is 101.2MPa/min. The basic processes of constructing SPT diagrams for the samples are given as follows:

- (i) Using the SCG parameter $n=13.83$ and $\sigma_0=48$ MPa in Equation (13), the equivalent stress that would result in the failure of the sample in 1 second is 51.33 MPa.
- (ii) Combination of this stress and $1-F=1/e$ (corresponding to the characteristic strength σ_0), where F is failure probability, gives the first data point of the 1 second line on the SPT diagram.

- (iii) Plot the 1 second line with a slope of Weibull parameter 5.5.
- (iv) A series of lines parallel to this line, with spacing between the lines equalling to $(\ln 10)/n$ or $2.3/n$. Each line represents a decade increase in life time.

Some selected prediction lines are shown in Figure 9

On the basis of the SPT diagram in Figure 9, the stress for a tolerable failure probability can be predictable; for example, the stress for a lifetime of 40 years should not exceed 4.53 ± 0.39 MPa to assure a failure probability below 1% at 800 °C. This implies that the applied stress which imposes on the membranes should not be beyond this value at 800 °C.

3.5 Discussion

As discussed previously, the SCG parameter n characterises the resistance of a material to SCG. A high value of n is usually interpreted as a low susceptibility to SCG. The high value of $n(24.32)$ at room temperature indicates that BSCF is not very susceptible to slow crack growth, which is in a good agreement with the findings of other groups[36]. However, the value of n of BSCF decreases dramatically to 13.83 as temperature rises to 800°C, which is approximately 43% of the value at room temperature. A similar trend has been also found in other perovskite-structured materials[35]. It indicates that BSCF is much more sensitive to SCG at 800°C. There can be several possible contributions to this phenomenon. The main possible reason is the reduction in chemical bonding energy at high temperature. The other possible

reasons are related to the secondary phase along grain boundary and the formation of oxygen vacancies in the grain bulk, which will be studied and discussed below.

As shown in Figure 10(A), only cubic phase has been detected by XRD in all specimens. However, the diffraction peaks of BSCF samples shift to large 2theta angles after testing at 800°C [as exemplified by the (110) peak position shown in Figure 10(B)], which indicates that the lattice parameter has decreased after exposure at 800°C.

EDS linescans across 20 grain boundaries show that the bulk oxygen content in the samples tested at RT(50.4 ± 0.1 at.%) is slightly higher than that in the samples tested at 800°C(49.3 ± 0.2 at.%) in Figure 11. However, it is clearly observed in Figure 11 (B) there is an increase in oxygen and a decrease in cations at grain boundaries at 800°C. In combination with XRD analysis, it suggests that oxygen vacancies are formed in the grain bulk possibly due to the diffusion of oxygen ions from grain bulk to grain boundary. In addition, EDS linescans are recorded to quantitatively analyse the composition of the grain boundary phase and the grain bulk. The compositions are given in Table 1. The ratio of Ba-, Sr-, Co-, Fe-, and O- concentrations along a linescan across the grain boundary is around 12.6:12.4:20:5:50 at RT while the ratio of these compositions is approximate 10:10:16:4:60 after testing at 800 °C. According to the previous investigation, Švarcová *et al.*[37] have demonstrated that the ratio of Ba-, Sr-, Co-, Fe-, and O- concentrations 10:10:16:4:60 exhibits a hexagonal structure. And other groups[38] have reported that in terms of BSCF annealed at 800°C, a

cubic-to-hexagonal phase transition can be found at grain boundary. It suggests that the grain boundary phase possibly exhibits hexagonal structure.

It has been reported by Evans *et al.*[39]that grain boundary phases can be in response to the strength degradation and the decrease in the slow crack growth parameter n . Additionally, oxygen vacancies can also result in the strength degradation at high temperature due to the decrease in bond strength[40]. As seen in Figure 12, it shows the existence of secondary phases at the grain boundaries in the interior of the bulk. Therefore, thermally activation bond rupture, grain boundary phase and oxygen vacancies can be the reasons for the reduction in the value of n at 800°C.

4 Conclusion

The SCG behaviour of BSCF was investigated by a constant load method and constant stress rate method at RT and 800°C, respectively. The SCG parameter n was determined to be 24.32 and 13.83 at RT and 800°C in air, respectively. It indicates that BSCF is more susceptible to SCG at 800°C. This can be attributed by thermally activation bond rupture, grain boundary phase and oxygen vacancies. The strength-probability-time (SPT) diagram is constructed for design proposes. The stress for a lifetime of 40 years should not exceed 27.21 and 4.53 MPa to assure a failure probability below 1% at RT and 800°C, respectively. Studies of mechanical properties at high temperatures will be conducted in future to provide more relevant information for the operation conditions of BSCF as a membrane material

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FIGURE 1 SEM image of the fracture surface after ring-on-ring bending tests. Fracture originated from the indentation-induced cracks

FIGURE 2 (A) Crack tip at time t_1 , (B) crack growth under constant loading at time t_2

FIGURE 3 Crack growth of BSCF as a function of stress intensity factor determined by ring-on-ring bending tests and compact tension tests. This blue line is a guide to the eye

FIGURE 4 Crack blunting was observed when crack propagated at (A) time t1 and (B) time t2

FIGURE 5 Crack branching was observed when crack propagated at (A) time t1 and (B) time t2

FIGURE 6 Crack branching observed in the interior of the bulk

FIGURE 7 Fracture stress of BSCF determined by ring-on-ring bending tests as a function of stress rate (log-log plot) at 800°C

FIGURE 8 Strength-probability-time diagram for the BSCF tested at RT

FIGURE 9 Strength-probability-time diagram for the BSCF tested at 800°C

FIGURE 10 (A) XRD patterns of fractured BSCF samples under different conditions; (B) Refined XRD patterns of the main peak (110) of fractured BSCF samples

FIGURE 11 EDS linescans across the grain boundary of fractured BSCF samples: (A) 101.2 MPa/min at RT; (B) 0.1012 MPa/min at 800°C

FIGURE 12 Grain boundary phase was observed in the interior of the BSCF bulk at 800°C by FIB

TABLE 1 The content of elements (BSCF) at RT and 800°C

Element	Atomic %	
	At RT	At 800°C
Ba	12.6 ± 0.1	10.3 ± 0.2
Sr	12.4 ± 0.1	9.7 ± 0.1
Co	20.0 ± 0.2	15.9 ± 0.1
Fe	5.1 ± 0.1	4.0 ± 0.1
O	49.9 ± 0.2	60.0 ± 0.2