Slow Crack Growth and Creep Rupture of \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 - \delta \)

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**Abstract.** \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 - \delta \) is a mixed ion-electron conductor with high application potential as high-temperature gas separation membrane. However, in practical use the integrity of this brittle perovskite is challenged by the mechanical boundary conditions of transient temperature exposure. Moreover, long term failure mechanisms such as static fatigue at room temperature and creep rupture at operation temperature might occur. The relevance of both effects for BSCF has been investigated. The slow crack growth at room temperature has been determined using bi-axial bending under different loading rates. The creep rupture at elevated temperature has been analyzed from three-point bending tests. The results indicate favourable behaviour of BSCF in both cases. A low risk of failure due to slow crack growth exists and the strain to failure in combined tensile-compressive mode reaches up to 40%.

**Introduction**

Based on the growing awareness to the long term climatic development the reduction of carbon dioxide emission has received increasing attention [1]. One of the most promising options to separate carbon dioxide in fossil power plants is the oxy-fuel combustion, where ceramic gas separation membranes provide the necessary oxygen [1]. Various mixed ion electron conducting (MIEC) perovskites have been suggested as possible oxygen transport membranes (OTMs). In particular \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 - \delta \) (BSCF) with its high oxygen permeation rate appears to be one of the most promising OTM materials [2].

Under the severe conditions of real application the materials stability is challenged by the high operation temperature, pressure gradients across the membrane and chemically induced strains. In addition to microstructural stability the mechanical integrity is a main requirement to warrant the long term functionality [3]. Actually the long-term performance of a ceramic component does not only rely upon the initial strength and fracture toughness of the material, but also depends on the long-term failure behaviour. Slow crack growth (SCG) of the component might be important at ambient temperature. SCG is generally not well addressed for perovskite type ceramic membrane materials. For the perovskite \( \text{La}_{0.2}\text{Sr}_{0.8}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3 - \delta \) (LSFC) SCG has been investigated [Fehler! Textmarke nicht definiert., 4]. The SCG is investigated in the present work measuring the stress rate dependence of the fracture strength [5]. Stress rate effects are important to evaluate the effect of thermally induced stresses, which can be generated by differences in components thermal expansion or temperature gradients and hence the rate of temperature changes during start-up and shut-down.

Long-term failure might also occur at the elevated operation temperature due to creep. Previous investigations on BSCF creep concentrated mainly on the deformation under compressive loads [6,7]. Between 600 °C and 800 °C the compressive creep rates of BSCF in air were almost constant but increased continuously up to 900 °C [7]. Since during operation tensile as well as compressive stresses act on OTM components an important thermo-mechanical aspect at elevated temperatures is also the creep rupture under tensile or combined tensile-compressive loads. Recently reported C-ring creep tests revealed the formation of pores along grain boundaries normal to the tensile stresses that ultimately lead to creep rupture [7]. In fact the authors estimated a critical strain of \( \sim 0.2 \% \) for damage initiation under tensile loading of a C-ring specimen. Note that acceptable creep rates in a
compressive mode for engineering ceramics are suggested to be about $10^{-10} \text{ s}^{-1}$ yielding a tolerable strain of about 1% per year. The creep is analysed in 3-point bending.

**Experimental**

Disk-shaped (for SCG test, 22 mm × 2 mm) specimens were provided by Fraunhofer IKTS, Institutsteil Hermsdorf and bar geometry specimens (for creep test, 30 mm × 4 mm × 3 mm) were provided by IEK-1, Forschungszentrum Jülich GmbH. The initial powders were supplied by Treibacher Industrie AG, Austria. The powders were uniaxially pressed with a pressure of 105 MPa and sintered at 1000 °C for 12 h at a heating rate of 5 K/min and a cooling rate of 0.5 K/min. Some bar-shaped specimens received additional polishing to permit an optical measurement of the strain.

The slow crack growth was tested using biaxial bending under different loading rates at room temperature. The ring-on-ring bending test followed the procedures recommended in the ASTM C 1499-05. The experiments for the SCG analysis were performed with applied stress rates from 10 tests each at $3.2 \cdot 10^{-3}$, $3.2 \cdot 10^{-2}$, 3.2 MPa/s and 25 tests at $3.2 \cdot 10^{-1}$ MPa, thus permitting a rather accurate determination of the Weibull modulus following ASTM C1239-07.

The creep failure was investigated in a three-point bending arrangement. The tests were carried out up to failure between 850 and 900 °C in air (at 800 °C the creep rate was too low to reach failure relevant specimen deformations in a finite time). Note that these temperatures are also in the proposed operation range of gas separation membranes [1]. The three-point bending test followed the procedures recommended in ASTM C1-161. For the tests at elevated temperatures, a heating rate of 2 K/min was used. At higher temperatures a dwell time of 1 h was chosen to reach thermal equilibrium before testing. For some of the specimens the creep strain was measured directly using the change of distance between hardness impressions [13, 14] as illustrated in Fig. 1. The indentation marks were imprinted with a Fischer HC100 indentation system applying a load of 1N.

![Fig. 1: a) Schematic drawing of the direct strain measurement using the change in position of hardness impressions, b) rows of imprints (load 1 N).](image-url)
Results and discussion

Slow crack growth (SCG). The fracture stress values were analysed statistically to determine characteristic strength and Weibull modulus. The loading rate sensitivity of bending test data can be used to assess the slow crack growth sensitivity of a material. It has been shown that the strength is linked to a particular stress rate $\sigma$ via [4,5]:

$$\sigma_f = \frac{1}{n+1} \log \sigma + \log D.$$  \hfill (1)

where $n$ and $D$ are the SCG parameters. Fig. 2 gives a graphical representation of the data for BSCF. The resulting SCG parameters are $n \sim 30$ and $D \sim 94$ MPa, which compares well to the literature data of LSFC ($n = 24$, $D = 95$ MPa), another perovskite material considered for OTM application [4]. For both perovskites the crack kinetics parameter $n$ is too high to expect pronounced SCG. For comparison much lower values of $n \sim 11 - 18$ have been reported for soda lime glass, a material prone to static fatigue [5].

![Fig. 2: Fracture strength as a function of stress rate. The line is a linear regression result.](image)

Creep rupture. 3-point bending creep tests have been carried out at 850 and 900 °C. No significant creep occurred at 800 °C and below in agreement with the reported low compressive creep rate for this material [6,7]. The resulting creep rupture time as a function of the nominal applied stress is given in Fig. 3. The time to creep failure decreases with temperature and applied nominal stress. It can be seen that increasing the temperature by 50 °C decreases the time to failure by a factor of $\sim 5 - 10$.

![Fig. 3: Rupture time as a function of nominal applied stress.](image)

Differences in creep rate under tensile and compressive load have been reported for ceramic materials in the past [13, 14]. Furthermore, although the simple three-point bending test permits to determine the rupture time as a function of the applied stress, it does not give information on the
failure strain. In order to determine this important parameter additional bending tests were performed where the strain distribution was measured microscopically by the change in distance between rows of hardness impressions in the cross-section (Fig. 1).

The tests were carried out at 900 °C with a nominal applied stress of 15 MPa. The distance between the rows of hardness impressions (initially ~120 µm) was re-measured after 25 h creep tests and then again after another additional 25 h under creep exposure. After the first 25 h of creep the direct strain measurement yielded a compressive strain of ~ -2 % and a tensile strain of 4.5 %. After the subsequent creep exposure the compressive strain remained almost unchanged at -2 %, whereas the tensile strain increased to almost 9 %. From the bending creep tests a compressive strain rate of $2 \cdot 10^{-7}$ s$^{-1}$ is determined for the first 25 hrs step, which is in agreement with literature data $3 \cdot 10^{-7}$ s$^{-1}$ for these conditions [6]. The tensile strain rate increases from $4.5 \cdot 10^{-7}$ s$^{-1}$ for the first annealing step to $9 \cdot 10^{-7}$ s$^{-1}$ after the additional 25 hrs exposure. Based on these results it can be estimated that the specimen that failed under identical conditions after ~ 210 h obtained a fracture strain of ~ 40 %.

Conclusions

The slow crack growth at room temperature was tested using biaxial bending under different loading rates. The results indicate a low risk of failure due to slow crack growth. A strength-probability-time analysis for a failure probability of 1% yields a tolerable stress limit of 28 MPa to warrant a lifetime of 40 years. So stress exerted onto the membrane for example due to differences in thermal expansion of sealant materials should not exceed this value.

The creep rupture time at 850 and 900 °C was investigated using three-point bending tests. The creep rupture time decreases considerably with temperature and applied stress. A temperature increase by 50 K reduces the time to rupture by a factor of ~ 5 - 10. Under the combined tensile-compressive creep mode a failure strain of ~ 40 % was estimated, yielding ~ 40 years lifetime for a creep deformation of 1 % per year.

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References