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Mechanical properties and lifetime predictions for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane material

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The mixed ion–electron conductor $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ has a strong application potential as high-temperature gas separation membrane. However, for real components the mechanical integrity of this brittle perovskite ceramic will be challenged by the boundary conditions of transient and stationary temperature exposure. In particular, long-term failure mechanisms such as static fatigue at room temperature and creep rupture at operation temperature may occur. The relevance of both effects is assessed. The effect of slow crack growth at room temperature has been investigated using fracture stresses obtained in biaxial bending under different loading rates. The provided data permit to assess the fracture stresses for different loading rates. Furthermore, a strength–probability–time plot is derived that permits a prediction of the lifetime under static loading conditions and hence the long-term reliability at room temperature. The creep rupture at typical operating temperatures was analysed using three-point bending tests permitting a determination of the failure stress in this application-related combined tensile–compressive mode. The creep rupture data are described by a modified Monkman–Grant relationship.

1. Introduction

Based on the growing interest in long-term climate control the reduction of carbon dioxide emission from fossil power plants has attracted increasing attention [1]. One promising option for separating carbon dioxide in fossil power plants is the fuel combustion, which is performed with oxygen rather than air [1]. The necessary oxygen for this oxy-fuel process can be provided in principal very efficiently by ceramic gas separation membranes operating at high temperatures. Various mixed ion–electron conducting (MIEC) perovskites have been considered as possible oxygen transport membranes (OTMs). In particular the high oxygen permeation rate of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) makes it one of the most promising materials [2].

However, under the severe conditions of real application the stability of the material is challenged not only by the high operating temperature (~850 °C), but also by pressure gradients across the membrane and chemically induced strains. In addition to the microstructural stability, mechanical integrity, which has only received limited attention [3–5], is also a basic requirement for guaranteeing long-term functionality [6]. In fact, the long-term performance of the ceramic component not only depends on its initial strength and fracture toughness, but also on its long-term failure behaviour. In particular, environmentally enhanced crack propagation at a subcritical stress levels, referred to as slow crack growth (SCG), can be important at ambient temperature [7], since it can lead to a decrease of an in-service strength.

Whereas for the perovskite $La_{0.2}Sr_{0.8}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSFC) the effect of SCG has been investigated [7,8], no data are available for BSCF. In this study, we assessed SCG by measuring the stress rate dependence of the fracture strength [9]. The stress rate dependence is important, for example, to evaluate the effect of thermally induced stresses during start-up and shut-down. Mathematically the data can be described by a SCG model. In addition, for design purposes a strength–probability–time (SPT) [8,10] plot is derived.

Long-term failure at the elevated operating temperature on the other hand may occur due to creep rupture. Previous reports on the creep for BSCF mainly concentrated on the deformation under compressive loads [11,12]. Between 600 °C and 800 °C the compressive creep rates of BSCF in air were nearly constant and the creep rate increased continuously up to 900 °C [12].

The creep rupture under tensile or combined tensile–compressive loads is obviously an important thermo-mechanical aspect since during operation, both tensile and compressive stresses act on the membrane components. Recently reported C-ring creep tests showed the formation of pores along grain boundaries normal to the tensile stresses that ultimately might lead to creep rupture [12]. In fact, a critical strain of ~0.2% for damage initiation was estimated. Note that acceptable creep rates in a compressive mode for engineering ceramics were suggested to be about 10^{-10}/s yielding a tolerable strain level of about 1% per year [12].

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The slow crack growth analysis was made using the biaxial ring-on-ring test, whereas the creep rupture at typical operating temperatures was analysed using an uniaxial 3-point bending test in order to permit a clear localization of the maximum stress. The creep rupture data are also described by a modified Monkman–Grant relationship [13]. Hence, both lifetime related aspects are considered: failure under stress at room temperature and operation related temperatures.

2. Experimental

The effect of slow crack growth (SCG) at room temperature was tested with disk-shaped specimens in the as-sintered condition using biaxial bending tests under different loading rates. Disk-shaped (for SCG test, 22 mm × 2 mm) specimens were provided by Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), Hermsdorf branch of the institute. The powder of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was prepared by conventional mixed oxide route. The components $BaCO_3$, $SrCO_3$, Fe_2O_3 and Co_3O_4 were weighted in stoichiometric amounts, milled together for 2 h and calcined at 1000 °C for 2 h. After repeated milling the powder was dried, pressed to pellets (diameter ~12 mm) and sintered for 24 h at 1130 °C in air and cooled in air with a rate of 10 K/min. The average porosity was ~8% and the grain size 29 ± 11 μm.

The ring-on-ring bending test followed the procedure recommended in ASTM C 1499-05 (see also [14]). The experiments for the SCG analysis were carried out with applied stress rates from 4 tests at 3.2×10^{-3} MPa/s, 10 tests at 3.2×10^{-2} and 3.2×10^{-1} MPa, and 5 tests at 3.2 MPa/s, thus permitting an estimation of the Weibull modulus following ASTM C1239-07. The fracture stress was determined as:

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

where P is the load, t the thickness, ν the Poisson's ratio, and r_1, r_2 and r_3 are the radii of the loading ring, support ring and specimen, respectively. The fracture stress data σ were used to determine the characteristic strength σ_f and the Weibull modulus m using a maximum likelihood statistical analysis according to ASTM C1239-07 based on the relationship for the failure probability P_f:

$$P_f = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_f}\right)^m\right] \quad (2)$$

Parameters describing the Weibull modulus were calculated according to ISO standard 20501: 2003. The tests were carried out with universal testing machines (Instron 1362 series). The central displacement of the specimen was detected with a sensor in contact with the lower surface of the sample. The actual displacement value was measured with a ceramic extension rod attached to a linear variable differential transformer (Sangamo, LVDT, range ± 1 mm, precision 1.25 μm). The load was determined with a 1.5 kN load cell (Interface 1210 BLR).

The creep rupture at elevated temperatures was investigated on the basis of a three-point bending test arrangement (30 mm × 4 mm × 3 mm). All specimens were prepared from powders supplied by Treibacher Industrie AG, Austria. The powders were uniaxially pressed (pressure of 105 MPa) and then sintered at 1000 °C for 12 h (heating rate 5 K/min, cooling rate 0.5 K/min). The density of the as-received samples was determined to be 5.37 g/cm^3 with a porosity of 4.5%. Assuming a spherical geometry the average grain size of the equivalent diameter was 10.1 ± 4.3 μm.

The three-point bending test followed the procedure recommended in ASTM C1-161. The tests were carried out up to failure between 850 °C and 900 °C in air (at 800 °C the creep rate was too low to reach failure-related specimen deformations in a finite time). A heating rate of 2 K/min was used. A dwell time of 1 h was chosen to reach thermal equilibrium before testing. The temperature was monitored close to the outer specimen surface with a thermocouple. Note that these temperatures are also in the proposed operating range of gas separation membranes [1]. The specimens were tested in the as-sintered condition, only the front side of some of the bar-shaped samples were polished to permit an optical measurement of the strain directly using the change of distance between hardness impressions [15,16] as illustrated in Fig. 1. The indentation marks were imprinted with a Fischer HC100 indentation system (load of 1 N). In addition, scanning electronic microscopy (SEM LEO1530) was used to analyse the fracture surfaces and microstructure.

3. Results and discussion

3.1. Slow crack growth (SCG)

The fracture stress values at RT were analysed statistically to determine characteristic strength and Weibull modulus. The Weibull moduli for loading rates 3.2×10^{-3} MPa/s, 3.2×10^{-2}, 3.2×10^{-1} MPa and 3.2 MPa/s, were 5 ± 3, 6 ± 2, 7 ± 2 and 5 ± 2, respectively. The weighted mean was determined to be 6.2 ± 1.2 and the unbiased estimate showed 5.9, while the lower and upper confidence bounds showed 4.5 and 7.6, respectively. Due to high standard deviation, a Weibull modulus of 6 was used in the further analysis. Fractographic analysis revealed that volume defects were the failure origin (Fig. 2).

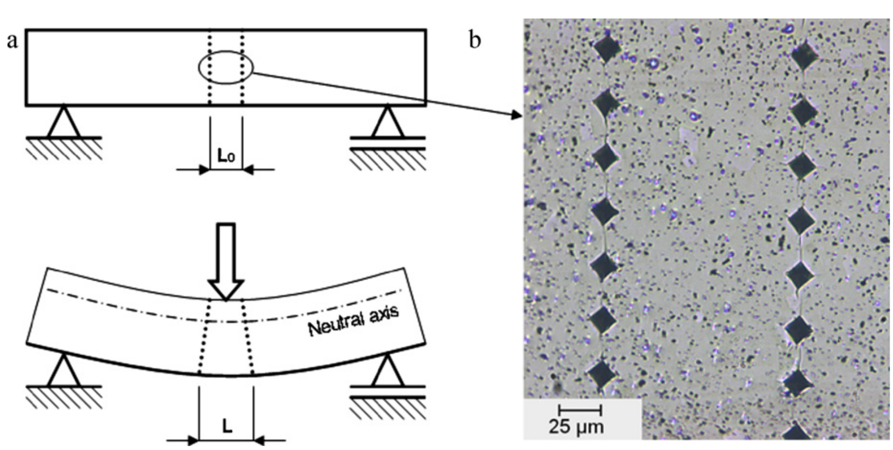

Fig. 1. (a) Schematic of the direct strain measurement using the change in position of hardness impressions, (b) rows of imprints (load 1 N).