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JECS-11191; No. of Pages 14
ARTICLE IN PRESS
Journal of the European Ceramic Society xxx (2017) xxx–xxx
Contents lists available at www.sciencedirect.com
Journal of the European Ceramic Society
journal homepage: www.elsevier.com/locate/jeurceramsoc

Determination of the bonding strength in solid oxide fuel cells' interfaces by Schwickerath crack initiation test

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ARTICLE INFO

Article history:
Received 19 November 2016
Received in revised form 5 April 2017
Accepted 7 April 2017
Available online xxx

Keywords:
Schwickerath crack-initiation test
Three-point bending test
SOFC interfaces
Metal-ceramic bond strength

ABSTRACT

An adaptation of the Schwickerath crack initiation test (ISO 9693) was used to determine the bonding strength between an anode support and three different cathodes with a solid oxide fuel cell interconnect. Interfacial elemental characterization of the interfaces was carried out by SEM/EDS analysis on fracture surfaces to investigate the bonding mechanisms. SEM/EDS of fresh fractures were also performed to determine the cohesion/adhesion mechanism of bonding. Calculations of the residual stresses were determined by finite element simulation using ANSYS, based on thermo-mechanical properties of the materials obtained by measurement, calculation or literature.

1. Introduction

The bonding between solid oxide fuel cell (SOFC) electrodes and metal interconnects is of utmost importance since it may determine overall stack lifetime [1–4]. Fig. 1 shows a mechanical failure of a real SOFC. It can be clearly seen the failure pattern: the crack kinking to the cathode side and propagating through the cathode material, kinking again to the interface and then back to the cathode, leaving cathode material on the interconnect.

A few authors have investigated the bonding strength of interconnect-cathode/anode interfaces in SOFCs following different techniques [5,6]. In this work, an adaptation of the Schwickerath crack initiation test (ISO 9693) (SCIT), introduced in 1999 for dental ceramic-metal composites, is proposed [7]. Despite that the geometries used in SOFCs are different, the ceramic and metal materials are similar (e.g. zirconia, stainless steel, etc.) and hence the bonding mechanisms are comparable. The failure pattern in SCIT tests performed here is similar to that found in real stacks (Fig. 1), supporting the relevance of the proposed method. Hence, the evaluation of the bonding strength could be performed using a similar approach.

The specimens investigated were tape cast SOFC cells. The bonds between SOFC cells and metal interconnects were obtained at high temperature and under loading conditions to simulate the real conditions used during stack assembly. Since both the cells and the IC/cell components to be tested are layered structures of different materials, residual stresses develop during sample preparation. Finite element (FE) modelling was employed in two stages, first to calculate the residual stresses after sintering and later to simulate the SCIT to obtain the strength of the interfaces from the experimentally accessible quantities. Nano-indentation testing performed in the cross-section of the samples was employed to determine the elastic properties of the materials forming the investigated interfaces. Finally, the failing interfaces were investigated by SEM and EDS.

2. Crack initiation test

2.1. Schwickerath crack initiation test (ISO 9693)

This three-point flexure bond test was proposed by Lenz et al. [8]. In the test (Fig. 2a), the critical bending force, F_{fail}, leading to debonding of the ceramic from the metal strip at one of the two ends of the ceramic layer, is measured. Lentz et al. [8] demonstrated that the normal stress σ_{yy} for pure external mechanical loading is tensile in the immediate vicinity of the interface between

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http://dx.doi.org/10.1016/j.jeurceramsoc.2017.04.018
0955-2219/

Please cite this article in press as: D.N. Boccaccini, et al., Determination of the bonding strength in solid oxide fuel cells' interfaces by Schwickerath crack initiation test, *J Eur Ceram Soc* (2017), http://dx.doi.org/10.1016/j.jeurceramsoc.2017.04.018

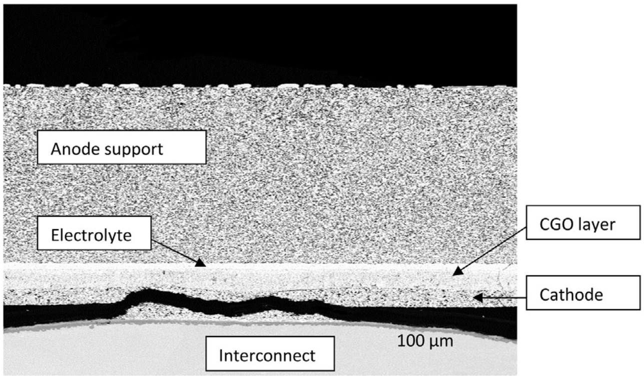

Fig. 1. SEM images of a loss of contact between interconnect and cell seen in a cross-section of SOFC stack after operation.

the steel and ceramics at the edge of the ceramic sample (point O, x = 0, in Fig. 2c and d) and becomes compressive along the x-axis (Fig. 2c and d) [8]. Further numerical simulations varying the Young's modulus of the metal E_M in a range ±10% revealed the remarkable result that the transition point of σ_{yy} from tension to compression is always located at x = x*, which is approximately at x = 0.2 mm in the case of pure external mechanical loading [8] and the prescribed dimensions of the sample in ISO 9693. Furthermore, Lentz at al. [8] demonstrated with a FE analysis, that, for a specimen having the dimensions specified in the ISO 9693 and with a Young's modulus within the complete range of values for dental alloys, the load stresses at the material interface in the region of initial debonding satisfy the condition $|\bar{\sigma}_{xy}/\bar{\sigma}_{yy}| \cong 1$ (where $|\bar{\sigma}_{xy}|$ and $|\bar{\sigma}_{yy}|$ are the mean shear and normal stresses, respectively). In terms of fracture mechanics, the interface at x = 0 is loaded by a superposition of crack opening mode I (tensile forces) and II (shear forces), both loads being of the same magnitude. They conclude that all metal-ceramic combinations will be tested under similar load stress conditions (combined shear and tensile loading of nearly identical magnitude). This is assuming that the residual stresses are negligible. The bonding strength (τ) (MPa) is defined in ISO 9693 as the absolute value of the mean shear stress $|\bar{\sigma}_{xy}|$ for a load of 1 N in the region of positive stress σ_{yy} (from x = 0 to x = x*), multiplied by F_{fail} [7].

$$\tau = \frac{|\bar{\sigma}_{xy}|}{1N} F_{fail} \tag{1}$$

The determination of the bonding strength by the ISO 9693 standard requires that the ratio $|\bar{\sigma}_{xy}/\bar{\sigma}_{yy}| \cong 1$ to ensure that all metal-ceramic combinations are tested under similar load stress conditions (combined shear and tensile loading of nearly identical magnitude) [9].

Swain et al. [10] report a fracture mechanics analysis of the test for the determination of important fracture mechanics parameters, i.e. energy release rate, etc. Although other methods, such as the Charalambides [11] method exists, these require larger areas to be bonded. This can be a challenge to manufacture given the strength of the bonds, why the Schwickerath specimens with smaller bonding area in this case are advantageous. All in all, this is the most used test in the scientific community for the determination of bonding strength in ceramic-metal interfaces. However, its application for the analysis of bonding in SOFC interfaces is relatively new [12].

2.2. Adapted Schwickerath crack initiation test for metal-ceramic SOFCs interfaces

In this work, the specifications established in the SCIT (ISO 9693) were adapted to the geometrical characteristics of the SOFC components to be investigated and to the three-point bending fixture employed. Fig. 2b) shows the test conditions employed in this paper.

FE analysis was employed to calculate residual stresses $\left(\sigma_{res_{xy}}, \sigma_{res_{yy}}\right)$ developed in the specimen (due to coefficient of thermal expansion (CTE) mismatch) during the cooling down, unlike the ISO 9693 standard, where the influence of the residual stresses in the bonding strength is not taken into account [7]. The FE model of the specimen (see Fig. 2c,d) is at first loaded decreasing the temperature from the bonding temperature of 930 °C to the testing temperature 20 °C (introducing residual stresses $\sigma_{res_{xy}}, \sigma_{res_{yy}}$) and then subjected to the effects of the actual loading at failure (F_{fail}) to calculate the stresses from external mechanical loading at the failure point $\left(\sigma_{ext_{xy}}, \sigma_{ext_{yy}}\right)$. These stresses $\left(\sigma_{res_{xy}}, \sigma_{res_{yy}}, \sigma_{ext_{xy}}, \sigma_{ext_{yy}}\right)$ are then introduced in Eq. (2) and (3) to determine the total stresses at the failure point $\left(\sigma_{xy}, \sigma_{yy}\right)$. Therefore, the bonding strength (τ) (MPa) is defined as the absolute value of the mean of the shear stresses $|\bar{\sigma}_{xy}|$ for a load of F = F_{fail} in the region of positive stress σ_{yy}, from x = 0 to x = x* (Eq. (4)), in a similar manner as in ISO 9693.

$$\sigma_{xy} = \sigma_{res_{xy}} + \sigma_{ext_{yy}} \tag{2}$$

$$\sigma_{yy} = \sigma_{res_{xy}} + \sigma_{ext_{yy}} \tag{3}$$

$$\tau = |\bar{\sigma}_{xy}| \tag{4}$$

3. Experimental

Four different interface configurations are investigated in this work:

Config. 1) Interconnect-LSM ($(La_{0.75}Sr_{0.25})_sMnO_3$) cathode contact layer with LSCF ($(La_{0.6}Sr_{0.4})_sCo_{0.2}Fe_{0.8}O_{3-\delta}$):CGO ($(Ce_{0.90}Gd_{0.10})O_{1.95}$) cathode; hereafter called (LSM:CGO)

Config. 2) Interconnect-LSC ($(La_{0.6}Sr_{0.4})_sCoO_{3-\delta}$):CGO cathode; hereafter called LSC:CGO

Config. 3) Interconnect-LSCF:CGO cathode; hereafter called LSCF:CGO and

Config. 4) Interconnect –3YSZ/Ni reduced anode support (hereafter called anode).

3.1. Materials

SOFC half-cells were manufactured and sintered following the standard procedure described by S. Linderoth [13].

The LSCF:CGO and LSC:CGO cathode mixtures were prepared in a proportion of 50%-50% wt. The cathode contact layer is made of pure LSM deposited onto a LSCF:CGO cathode material. They were deposited on the sintered half-cells by screen printing.

After the cathode deposition, the prepared cells were sintered [13], except the LSM cathode contact layer that was left in the green state. After the cathode deposition the average thickness of the cells was (0.4 ± 0.01) mm.

The interconnect is based on a 0.3 mm thick Crofer 22 APU stainless steel produced by Thyssen Krupp VDM, Germany.

3.2. Sample preparation

The samples consisted of various cell to interconnect assemblies with different cathode and anode materials interfacing the interconnect. Regarding the anode-interconnect configuration, the cell samples consist of half-cells (without cathode deposited), as these were bonded in hydrogen and the cathode materials will deteriorate through such a treatment.

The cells were laser cut to the dimension of (8 ± 0.1) mm × (3 ± 0.1) mm following the requirements of the ISO 9693 standard [7]. The SOFC interconnects (having a thickness of (0.3 ± 0.01) mm) were cut to dimensions (15 ± 0.1) mm × (3 ± 0.1) mm and bonded with the laser cut cells

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