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Residual stresses in suspension plasma sprayed electrolytes in metal-supported solid oxide fuel cell half cells

A. Macwan [a], D.L. Chen [a,*], M. Marr [b], O. Kesler [b]

[a] Department of Mechanical and Industrial Engineering, Ryerson University, 350 Victoria Street, Toronto, Ontario M5B 2K3, Canada
[b] Department of Mechanical and Industrial Engineering, University of Toronto, 5 King's College Road, Toronto, Ontario M5S 3G8, Canada

HIGHLIGHTS

- ► Yttria-stabilized zirconia (YSZ) electrolyte is made with suspension plasma spray.
- ► Residual stresses are evaluated via high-temperature X-ray diffractometry.
- ► Residual stresses in YSZ electrolyte layers are identified to be tensile in nature.
- ► With increasing temperature the residual stresses are observed to decrease.
- ► Torch power and stand-off distance have a strong effect on the residual stresses.

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ABSTRACT

Solid oxide fuel cells (SOFCs) efficiently convert chemical energy into electrical energy with fuel flexibility and low emissions. Plasma spraying has emerged as a fabrication technique for metal-supported SOFCs. Residual stresses in suspension plasma sprayed (SPS) yttria-stabilized zirconia (YSZ) electrolytes fabricated with various processing parameters and substrates were analyzed by X-ray diffraction. The temperature dependence of the residual stresses was also evaluated. The electrolyte residual stresses varied with both processing conditions and substrate characteristics, and ranged from 35 to 91 MPa. The change in stresses agreed well with the observed microstructural changes arising from the use of different processing conditions and substrates. The electrolytes fabricated using torch power and stand-off distance of 133 kW and 90 mm exhibited the highest residual stress due to the their relatively dense microstructure with low level of vertical cracking compared to electrolytes made with the other spray conditions. As these electrolytes were heated from room temperature to 750 °C, residual stresses decreased from 91 to 39 MPa. The decrease is due to changes in Young's modulus and to thermal expansion mismatch between the layers, and possibly also due to the formation of additional microcracks or creep of the porous stainless steel substrate.

1. Introduction

Extensive efforts to develop low-cost and reliable solid oxide fuel cells (SOFCs) for power generation and transportation applications are motivated by the pressing need for improved fuel efficiency, reduced anthropogenic greenhouse gas emissions, and enhanced energy security [1–6]. Currently, high material and production costs and poor durability are key barriers to the widespread commercialization of SOFCs [3,7,8]. One potential approach to reduce material costs and improve durability is to use a metal-supported cell structure based upon relatively inexpensive stainless steels [9,10]. The inclusion of stainless steels necessitates the use of intermediate operating temperatures (650–800 °C), but their high electrical and thermal conductivity, superior toughness and thermal shock resistance, and good workability are highly attractive attributes for SOFCs [11]. Thus, metal-supported SOFCs have recently received considerable attention [12–15].

When fabricating conventional anode-supported SOFCs, the electrolyte and electrode functional layers are typically deposited as wet ceramic powder slurries, which are then solidified by sintering at high temperatures. It is difficult to apply these wet ceramic fabrication methods to metal-supported SOFCs because the electrolyte sintering process could rapidly oxidize or densify the porous stainless steel supports. Alternatively, direct deposition fabrication methods such as plasma spraying may be better suited for the production of the functional layers in metal-supported SOFCs.

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[*] Corresponding author. Tel.: +1 416 979 5000x6487; fax: +1 416 979 5265.
E-mail address: dchen@ryerson.ca (D.L. Chen).

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In plasma spraying, feedstock powders are melted and accelerated by a plasma jet toward a substrate. Upon impact with the substrate, the molten particles flatten and solidify to form splats, which accumulate to form coating layers [16,17]. This process readily permits deposition of ceramic coatings on metallic supports without additional post-deposition heat treatment. As a rapid deposition process, plasma spraying could also reduce manufacturing costs, especially at low and intermediate volumes, compared to more time-consuming wet ceramic methods. Suspension plasma spraying (SPS) is a modification of the traditional plasma spray process in which the feedstock powders are suspended in liquid for feeding to the plasma rather than being fed as dry powders with the use of carrier gas. The suspension permits the use of smaller feedstock powders, so SPS could potentially be used to produce thinner coating layers and more refined microstructural features [18]. This study is focused on the electrolyte layer, which is made of 8 mol% yttria-stabilized zirconia (YSZ), and should be thin, dense, and gas-tight for good performance. As such, deposition of the electrolyte by SPS has been the subject of a number of studies [18,19].

One characteristic of plasma sprayed coatings is the presence of residual stresses, which originate from the large thermal gradients experienced during the deposition process. The residual stresses in plasma sprayed coatings can be sub-divided into two main contributions: quenching stress or primary stress, and thermal mismatch stress or secondary stress. The quenching stress arises as individual splats rapidly solidify and cool from a molten state to the substrate temperature, while their contraction is restricted by adhesion to the substrate. These quenching stresses are always tensile. Thermal mismatch stress develops during post-deposition cooling to room temperature due to the difference in the coefficients of thermal expansion (CTEs) between coating layers and substrate [20]. Thermal mismatch stress can be either tensile or compressive, depending on the relative values of the CTEs of the coating layers and substrate. In service, the applied stresses are superimposed on the residual stresses, which could increase or decrease the total stress, depending on the respective signs of each stress component. These stresses could increase the number and size of cracks in the electrolyte, which would reduce cell performance and could lead to catastrophic failure of the cell. Therefore, understanding the residual stresses arising from different processing conditions can provide useful insight into the mechanical integrity of the electrolyte prior to cell operation. Understanding residual stress may also provide useful insight toward modification of the spray process or cell design. For instance, the substrate temperature during spraying could be varied to alter quenching or thermal mismatch stresses, or the composition of the stainless steel support may be adjusted to change its thermal expansion behavior.

Since metal-supported SOFCs are operated in the 650–800 °C range, it is also of interest to ascertain residual stress values at these elevated temperatures in addition to at room temperature. Residual stress values at room and elevated temperatures in YSZ electrolytes in anode-supported or cathode-supported planar SOFCs fabricated by other processes have been previously reported [21–23]. However, to the authors' knowledge, no studies on the residual stresses in metal-supported planar SOFCs made by plasma spraying have been reported. The objective of the present study is, therefore, to identify the residual stresses of SPS YSZ electrolytes at room and elevated temperatures. The electrolytes were deposited on two types of substrates, one consisting of SOFC cathode layers on porous 430 stainless steel supports, and the other consisting of only the porous 430 stainless steel supports. Electrolytes made from various sets of spray parameters having a wide range of microstructural characteristics were tested to determine the effect of process conditions on residual stresses.

2. Experimental procedure

2.1. Plasma spray processing

The YSZ electrolyte coatings were deposited by SPS with an Axial III torch (Northwest Mettech Corp., North Vancouver, BC, Canada). Five different spray conditions, shown in Table 1, were selected. For all the spray conditions, an aqueous feedstock suspension of 8 mol% YSZ powder with a d_{50} of approximately 2.6 μm (Inframat Corp., Manchester, CT) was fed to the torch at a rate of 21 ml min^{-1}. The solid content of the suspension was 3 vol.% and polyethyleneimine was added as a dispersant. The suspension was injected axially into the plasma through a 0.84 mm ID syringe type injector, and 30 slpm N_2 was used as an atomizing gas. The substrates were preheated to ensure that their temperatures were at least 300 °C for the entire spray run, though depending on the spray conditions, peak substrate surface temperatures ranged from 430 to 770 °C. It was not possible to control substrate temperatures more precisely. The targeted thickness for all coatings was 50 μm, but the thickness of individual coatings ranged from 45 to 51 μm, except for the coatings fabricated using the G3 spray conditions, which had thicknesses of approximately 71 μm.

The electrolytes were deposited on two substrates. The LSM/YSZ + MG 2 substrates consisted of SOFC cathode layers on porous 430 stainless steel discs (Mott Corp., Farmington, CT) having a diameter of 25.4 mm and thickness of approximately 1.6 mm. The pore structure was designated as media grade (MG) 2, which indicates that only particles smaller than 2 μm should penetrate through the pore network if the discs were to be used as filters. The cathodes consisted of a composite of lanthanum strontium manganite (LSM) and YSZ and were previously deposited by plasma spraying, as described elsewhere [18]. The cathodes had an average thickness of approximately 40 μm. The electrolyte-cathode-support structure is often referred to as an SOFC "half cell". An SEM image of a cross-section of a sample half cell is shown in Fig. 1. The second substrates were simply porous 430 stainless steel discs (Mott Corp.) having a relatively fine MG 0.2 pore structure.

2.2. X-ray diffraction measurements

Residual stresses in the electrolytes were measured using X-ray diffraction (XRD). The residual stresses in electrolytes made with all 5 spray conditions on both substrates were measured at room temperature. Residual stresses in an electrolyte made with the G2 spray condition, which had a torch power of 133 kW and a stand-off

Table 1
Suspension plasma spray parameters used to deposit the YSZ electrolyte layers.

Identifier	G1	G2[a]	G3	G4	G5
Torch power, kW	133	133	133	100	162
Stand-off distance, mm	70	90	120	90	90
Plasma gas flow rate, slpm	275	275	275	275	275
Ar (%)	30	30	30	74	25
N_2 (%)	65	65	65	21	70
H_2 (%)	5	5	5	5	5
Current, A	600	600	600	600	750
Nozzle, mm	9.5 (3/8″)	9.5 (3/8″)	9.5 (3/8″)	9.5 (3/8″)	9.5 (3/8″)
Substrate	LSM/YSZ + MG 2/MG 0.2				

[a] Indicates the condition used to fabricate the electrolytes tested at elevated temperatures.