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Microstructure, hardness, and fracture toughness of suspension plasma sprayed yttria-stabilized zirconia electrolytes on stainless steel substrates

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ABSTRACT

Recent research interest in solid oxide fuel cells (SOFCs) has grown towards effective manufacturing processes that are compatible with low-cost materials such as stainless steel structural supports. Suspension plasma spraying is a promising technique that rapidly produces a fully consolidated, thin electrolyte layer with good microstructure control and without any post-deposition heat treatment. In the present study, suspension plasma spraying was used to deposit yttria-stabilized zirconia electrolyte coatings on porous stainless steel substrates using a range of spray conditions. Mechanical properties of the coatings, such as hardness and fracture toughness, were characterized. These properties can affect the durability of SOFC electrolytes, coupled with the thermal stresses generated during operation. Coating toughness and hardness were observed to be dependent on the torch power and stand-off distance during fabrication, which affect coating microstructural features such as porosity, microcracks, and segmentation cracks. The fracture toughness measured using an indentation technique of the coatings produced with a torch power of 133 kW and a stand-off distance of 90 mm was found to be 1.5 ± 0.15 MPa m$^{1/2}$.

1. Introduction

Solid-oxide fuel cells (SOFCs) are solid state electrochemical devices that convert chemical energy in fuels to electrical energy with high efficiency, low emissions, and fuel flexibility [1,2]. However, many challenges such as high material cost, high production cost, and poor durability limit their widespread commercialization [2,3]. Therefore, metal supported SOFCs have attracted significant interest due to several important advantages over conventional anode-, electrolyte-, or cathode-supported SOFCs, including their inexpensive metal supports and higher mechanical toughness [4–6]. The electrolyte layer conducts oxygen ions between the cathode and anode while also acting as a gas separation barrier. Therefore, it should be thin and dense to provide low ionic resistance and low gas permeability [7]. Electrolyte layers have previously been deposited using vacuum and low-pressure plasma spraying [8], high velocity oxy-fuel spraying [9], atmospheric powder plasma spraying [10], and suspension plasma spraying (SPS) [5,6,11].

SPS has been identified as a promising technique to deposit thin and dense electrolyte layers for SOFCs [4,5,12,13]. Since SPS uses feedstock powders suspended in a carrier liquid, it permits the use of finer powders, on the nano- or low micron scale, than conventional plasma spraying. Therefore, SPS can potentially produce thinner gas-tight coatings compared to other thermal spray techniques used to fabricate electrolytes in atmospheric conditions [4,5].

One issue in the fabrication of SPS coatings lies in the presence of residual stresses generated due to the large thermal gradients experienced during the process. Quenching and thermal mismatch stresses are the two main contributors to the overall residual stress. When molten powder particles strike the substrate, they are rapidly solidified and quenched to the substrate surface temperature, causing local tensile residual stresses in the splats that can be partially relieved by microcrack formation. After deposition, the coating is cooled to room temperature while its contraction is constrained by adhesion to the substrate, introducing additional thermal mismatch stresses to the quenching stresses [14]. In the present case, thermal mismatch stresses developed in the electrolyte during cooling from the deposition temperature to ambient temperature are compressive, as the coefficient of thermal expansion of yttria stabilized zirconia (YSZ) is lower than that of the porous stainless steel substrate ($\mathrm{TEC_{YSZ}}$-10.5 ppm K^{-1} < $\mathrm{TEC_{430L}}$-11.4 ppm K^{-1}) [15,16]. Residual stresses affect the coating mechanical properties and integrity. In addition, these stresses are affected by microstructural attributes such as cracks and porosity. As a result, it is

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important to understand the connection between process parameters, microstructure, residual stress, and mechanical properties of the coating. Moreover, the reliability and durability of SPS YSZ coatings depend in part on their cohesive and adhesive strength.

Suspension plasma spraying used to produce YSZ coatings has been studied by a number of authors. Marr and Kesler [7] made YSZ electrolyte coatings using SPS on stainless steel substrate and observed that higher torch powers and shorter stand-off distances produce denser and better-adhered coatings. Latka *et al.* [17] sprayed $ZrO_2 + 8$ wt.% Y_2O_3 (8YSZ) coatings using SPS on stainless steel substrate and showed that Martens macroharness decreases with increasing spray distance. Also, Wang *et al.* [11] observed that a higher input torch power produces a denser SPS YSZ coating on Ni–Cr–Fe–Mo alloy substrates. In our previous study, the effects of torch power and stand-off distance on the residual stresses and coating microstructure were studied, aiming to identify an optimum process condition [6]. The purpose of the present study was to identify the effects of SPS process parameters, i.e., torch power and stand-off distance, on the microhardness and coating and interfacial fracture toughness (cohesive and adhesive strengths) of 8 mol.% YSZ coatings on porous 430 stainless steel substrates.

2. Experimental procedure

SPS with an Axial III torch (Northwest Mettech Corp., North Vancouver, BC, Canada) was used to deposit YSZ coatings on porous stainless steel substrates using a range of spray conditions, as indicated in Table 1. More details about the procedure used are presented in [6]. The thickness of most individual coatings ranged from 40 to 45 μm, except for the D_{120}/P_{133} spray condition coatings (Table 1), which had an average thickness of 60 μm. The substrates were porous 430 stainless steel discs (Mott Corp., Farmington, CT) having a diameter of 25.4 mm and a thickness of approximately 1.6 mm. A typical cross-sectional SEM image of a coated substrate is shown in Fig. 1. The polished cross-sections were examined using a scanning electron microscope (SEM) (JEOL, JSM-6380LV, Tokyo, Japan) at an operating voltage of 20 kV. The porosity (volume fraction) was determined from polished cross-sections using image analysis. To determine representative porosity values, a series of SEM images with magnification of 3000× was obtained for individual specimens. For each coating, 5 images were randomly selected and an average value of porosity was calculated.

Phase analysis of the YSZ powder and coatings was performed using a PANalytical X'pert PRO MRD (PANalytical B.V., Almelo, Netherlands) high-resolution X-ray diffractometer using Cu-Kα radiation. The phase identification was performed at diffraction angles (2θ) ranging from 20° to 90° at a scan speed of 0.05°/s. Vickers microhardness tests were performed on polished cross-sections using a computerized Buehler microhardness testing machine, using a load of 100 g for 15 s. Approximately ten indentations were made randomly and used to calculate the average coating hardness. Fracture toughness measurements were made using the Vickers indentation technique. The principle of this method is based on the ability of coatings to inhibit crack propagation. The relationship between fracture toughness, K_c, and crack length c is presented in Eq. (1) [18]:

$$K_c = \alpha\left(\frac{E}{H}\right)^{1/2}\frac{P}{c^{3/2}}, \qquad (1)$$

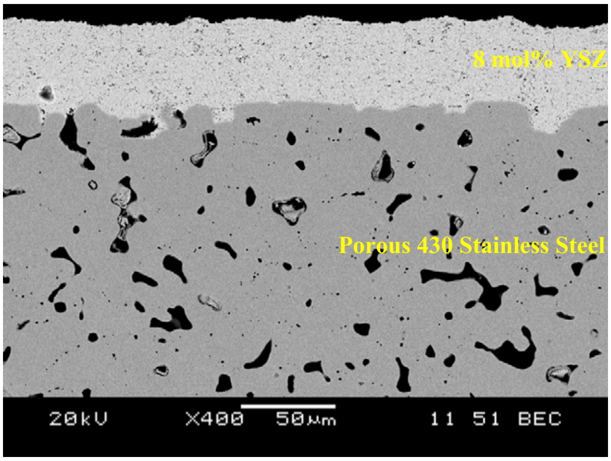

Fig. 1. Typical cross-sectional SEM image of a coated substrate.

where P is the peak load during indentation, E is the Young's modulus, H is the Vickers hardness, and α is an empirical constant that depends on the geometry of the indenter. $\alpha = 0.016$ for both Berkovich and Vickers type indenters. To satisfy a geometrical requirement for the complete formation of a “half-penny” cracking pattern, it is required that $c \geq 2a$, where a is the radius of the impression [18]. The fracture toughness of a coating with residual stresses σ can be calculated using Eq. (2) [18,19]:

$$K_c = \alpha\left(\frac{E}{H}\right)^{1/2}\frac{P}{c^{3/2}} + Z\sigma_r c^{1/2}, \qquad (2)$$

where Z is a crack shape factor given by Eq. (3) [18,19].

$$Z = 1.12\sqrt{\pi}\frac{b/c}{\left(\frac{3\pi}{8}\right) + \left(\frac{\pi}{8}\right)(b/c)^2}, \qquad (3)$$

where b is the depth of the crack and c is its length. $Z = 1.26$ for an idealized half-penny, i.e., when $b = c$. To meet the geometrical requirements for using Eqs. (1) or (2), the indentation depth (which is smaller than the depth b of the crack induced) should be much less than 10% of the coating thickness. A Vickers microhardness tester was used to make an indentation on the polished top surface of the coatings. A load of 200 g and dwell time of 15 s were used for the tests. SEM observations were carried out to measure the crack length for each indentation, and the reported values each represent an average of 15 measurements.

The interfacial fracture toughness of the coatings was evaluated from a Vickers interface indentation test [20]. The indentations were located on the cross-section at the coating–substrate interface of the coating fabricated using the optimal fabrication condition (D_{90}/P_{133}), using a Vickers microhardness tester (Micromet-5100) with loads of 50 g, 100 g and 200 g and a dwell time of 15 s. Five indentations were made at each level of load in order to determine the mean crack length. The diagonal of the indent was carefully located to coincide with the coating–substrate interface. The indentations were examined by SEM.

Table 1
Suspension plasma spraying process parameters used to deposit YSZ coatings on porous stainless steel substrates.

Spray condition	Plasma gas flow rate (slpm)	Plasma gas composition (%)	Nozzle diameter (mm)	Current (A)	Stand-off distance (mm)	Torch power (kW)
D_{70}/P_{133}	275	30Ar, 65N_2, 5H_2	9.53	600	70	133
D_{90}/P_{133}	275	30Ar, 65N_2, 5H_2	9.53	600	90	133
D_{120}/P_{133}	275	30Ar, 65N_2, 5H_2	9.53	600	120	133
D_{90}/P_{100}	275	74Ar, 21N_2, 5H_2	9.53	600	90	100
D_{90}/P_{162}	275	25Ar, 70N_2, 5H_2	9.53	750	90	162