

Particle states in plasma and their effects on properties of Ni/YSZ spray coatings for SOFC anode applications.

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A process of atmospheric plasma spray (APS) deposition has been developed for the deposition of high performance anode coatings, which are essential for achieving high power density in solid oxide fuel cells (SOFC). This research studies new feedstock materials, including nano-components of NiO and YSZ (300 nm), obtained through a spray drying method. Nano-crystalline powder, YSZ_{40 vol%} NiO_{30 vol%} Graphite_{30 vol%}, has been synthesized by a spray drying method using a combination of polyvinyl alcohol and polyvinyl pyrrolidone. Morphological analysis of the coating at different hydrogen gas flow rates was done with a scanning electron microscope (SEM). The oxidation and decomposition behaviors of the coatings were studied by TG/DTA analysis. Thermo-gravimetric results giving the reduction of graphite during the spray process showed that the change in mass of the coating is less than that of the powder. The microhardness and electrical conductivity of the spray coatings were measured using the Vickers hardness and four-probe DC method. A maximum electrical conductivity of 651 S/cm at 800 °C was achieved, which is higher than the standard required value of 160 S/cm.

Key words: Solid oxide fuel cell (SOFC), Plasma deposition, Ni–YSZ cermet, Thermal analysis.

Introduction

A solid oxide fuel cell (SOFC) is a ceramic device which directly converts the chemical energies of fuel and oxidant gases into electrical energy without using combustion as an intermediate step [1, 2]. In general, a single fuel cell consists of two porous electrodes (anode and cathode) separated by a dense and gas tight electrolyte. Among all the components in an SOFC, the anode plays the most important role in the oxidation of the fuel, the process which generates electricity. Nickel/Yttria Stabilized Zirconia (YSZ) cermets using the 8YSZ framework are good ionic conductors, with a Ni dispersion as the conducting mechanism. This is the most common anode material for SOFC applications because of its low cost and relatively high electro-catalytic activity (low charge transfer resistance) [3–8]. In general, the percolation threshold for conductivity in Ni/YSZ cermets is about 30 vol% Ni content, above which the conductivity is sharply increased [3]. However, the conductivity is also influenced by the microstructural characteristics of the anode, such as its porosity, pore size distribution, and feedstock powder size, as well as the conductivity of each component. Lee et al. have indicated that, considering the contiguity effect, the Ni content should remain below 50 vol% [8]. High porosity is required for the SOFC anode layer to supply fuel,

remove reaction products, and to maintain a three-phase boundary (TPB - electrolyte, electrode, and gas phase), which acts as an active electrochemical site for reaction. Hence, microstructural control of the anode is important in improving the SOFC's efficiency. NiO/YSZ anode materials are usually prepared by the mechanical mixing of commercially available NiO and YSZ powders. This method produces a non-uniform distribution of the Ni phase in the cermets, leading to poor performance. Therefore, several wet chemical processes such as sol-gel [9, 10], complex formation with chelating agents [11], spray pyrolysis of a slurry YSZ in nickel acetate solution [12], and the mechano-fusion process [13] have been reported. Other processes such as vapor deposition [14] and the spraying of wet powder [15] have also been reported. The focus of these efforts is either to prepare a homogeneous nanoscale mixture of NiO and YSZ, or to produce fine YSZ particles covered in submicrometer NiO composite powders.

Spray drying is a process by which a fluid feed material is transformed into a dry powder by spraying the feed into a hot medium. The feed materials are either water-based suspensions with air as the drying gas, or organic solvent-based suspensions (usually ethanol) with nitrogen as the drying gas [16]. The ideal microstructure of the SOFC anode can be manufactured by many methods such as tape casting, screen printing, slurry coating, and PVD. The thermal spray technique, especially the atmospheric plasma spray technique (APS) [17], is an economically attractive and effective technique for the industrial production of SOFCs because of its low cost, easy operation, high deposition efficiency, and wide selection of materials. [18].

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An anode coating requires phase stability in the fuel environment, adequate porosity for gas transport, matching of its thermal expansion coefficient with the other components in the cell, and high electrical conductivity. Triple phase boundaries in the coating are required to obtain high conductivity.

In anode-supported SOFCs, the anode is the substrate of the whole cell, and plays the most important role in the oxidation of fuel. A Ni/YSZ cermet is the most common anode material for SOFC applications because of its low cost and the matching of its thermal expansion coefficient with other cell components.

In this study, 8YSZ:NiO:graphite (40 vol%:30 vol%:30 vol%) spray dried powders were thermal spray deposited on a porous metallic substrate. The change in state of the particles in the plasma is discussed along with the microstructure, thermal analysis, microhardness and electrical conductivity results.

Experiments

The spray dried powders used for this experiment consisted of YSZ, NiO, and graphite. YSZ (40 vol%), NiO (30 vol%), and graphite (30 vol%) nano-powders (300 nm) were ball milled for 12 hours. Nano-sized powders cannot be successfully plasma sprayed as each particle has different trajectories in the plasma flame during flight. To avoid this, the powders were reconstituted with a spray drying method [19].

The slurry was prepared through the addition of 500 g of YSZ-NiO-graphite mixing powder to distilled water (1l) in which 2 g of the dispersant (binder) solution was added. The slurry was ball-milled with a zirconia grinding media for 12 hours. Then, 2 g of the binder solution was added and milling was continued for another 4 hours. The spray drying process was carried out at 250 °C in a pilot spray drier. The binders used for the process were PVA (Polyvinyl alcohol) MW 89,000-98,000 (1 g), PVP (Polyvinyl pyrrolidone) MW 40,000 (1 g), and PEG (Polyethylene glycol) MW 20,000 (0.5 g). The inlet temperature was 240 °C, the outlet temperature was 110 °C, the atomizer speed was 8,000 rpm, and the slurry feeding rate was 3 l h⁻¹. The heat treatment of the powder was carried out in a furnace with an argon environment for good compaction between the phases.

Before spraying, characterization of the nano-structured spray dried powder feedstock was performed using SEM analysis.

Fig. 1 shows SEM images of each feedstock phase of the spray dried powder. In Fig. 1(a), 1(b), and 1(c) are the SEM images of the individual YSZ, NiO, and graphite powders. It is seen that YSZ has a spherical morphology, and the NiO powder is fractured. The morphology of the graphite powder is nearly spherical. Fig. 1(d) shows the morphology of the spray dried powders. It is shown in Fig. 1(d) that the spray dried powders are nearly uniform in size and all have spherical morphology.

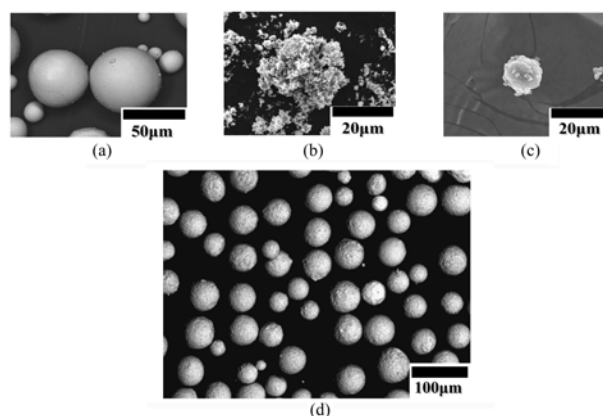


Fig. 1. SEM images of the feedstock materials.

It is well known that the packing density of nano-sized materials is higher than that of micro-sized materials because of their high surface energies and the effects of Van der Waals forces. The spray dried powders were sintered at 1,000 °C for 4 hours under a flowing atmosphere of 6 vol% H₂/N₂ to increase the cohesiveness of the powder.

It is easy and cost effective to fabricate the coating using the APS technique. The shape of the substrate does not affect the quality of the results, so planar, tubular, and single chambers can be coated, and large areas can be covered. Hence the APS technique has been selected for use in these experiments. The coatings were prepared from the blended and nano-structured spray dried composite powder feedstocks with a DC atmospheric plasma spray system (Sulzer Metco 9 MB). The APS system consists of a DC plasma torch that generates a high temperature plasma flame under atmospheric conditions, a powder feeder for delivering plasma sprayable powders, and a cooling system for the torch. The plasma process gas used for this experiment was a mixture of argon and hydrogen. The spraying distance between the substrate and the centerline of the nozzle was 100 mm. The feedstock powder was vertically injected into the plasma gas downstream from the plasma jet centerline at a feed rate of 20 g minute⁻¹. The powder was injected into the plasma jet at a 45° angle against the vertical centerline of the nozzle to minimize the effects of gravitational forces on the powder's trajectory. A porous metallic weave mesh was used as the substrate which is the conventional way to reduce the size and weight of the substrate. This was spot welded, and was then grit blasted and cleaned ultrasonically waves before spraying.

In order to change the characteristics of the plasma jet, the hydrogen gas flow rate was altered while the other process parameters were kept constant. The processing parameters are shown in Table 1.

The microstructure of the coatings was observed through a SEM. The thermal behavior of the powders and coatings was studied with a TG/DTA thermal analyzer at a temperature range of 20 °C-1,000 °C, with a heating rate of 10 K minute⁻¹ in an oxygen atmosphere. The oxygen flow

Table 1. The APS process parameters

Plasma Gas Composition		Arc Current [A]	TBD Distance [mm]	Powder Feed Rate [g minute ⁻¹]
Ar [SCFH]	H ₂ [SCFH]			
100	5/10/15	500	100	20

* SCFH: Cubic feet per hour at standard conditions
(1 SCFH 0.47 = 1 pm).

rate was 100 ml minute⁻¹. Vickers micro-hardness measurements were conducted on polished cross-sectional surfaces using a Vickers indenter with an applied load of 2.942 N. Electrical resistance was measured with the DC 4 probe method using platinum wires, a current source (Keithley 224), and a multimeter (Keithley 2000) under a flow of 4 vol% of H₂/Ar. The gas flow rate was 150 ml minute⁻¹. The samples were heated to 1,000 °C at a heating rate of 10 K minute⁻¹, and held at a constant temperature for 30 minute. The measurements were performed upon cooling.

Results and discussion

The sprayed coatings were polished and then characterized through a SEM to study their microstructural characteristics. The average thickness of the coating was 150 µm. Fig. 2 shows SEM images of the sprayed coatings prepared from NiO/YSZ/graphite spray dried powders at different hydrogen gas (secondary gas) flow rates. It can be seen in Fig. 2(a) that some of the particles are not fully melted. Many unmelted, and some partially melted, powder particles are embedded in the coating. The black spots in the images are pores. Figs. 2(b), 2(c) show the SEM images

of the coatings prepared using 10 SCFH (1 SCFH = 0.47 lpm) and 15 SCFH hydrogen flow rates. At the 10 SCFH hydrogen gas flow rate, all the powders are melted or partially melted, and the porosity distribution is reduced as compared with Fig. 2(a). At the 15 SCFH hydrogen gas flow rate, all the powders were melted due to the high enthalpy and the heat flux of the plasma jet. Fig. 2(c) shows that all the powders were melted and a uniform coating morphology was obtained using the 15 SCFH hydrogen flow. Increasing the hydrogen gas flow rate, enthalpy and the heat flux supplied to the powders in the plasma are increased because hydrogen is a diatomic gas. This leads to complete melting and coating formation. The porosity distribution is also uniform under higher hydrogen gas flow rates. The coating exhibits a layer microstructure.

Figs. 3(a), 3(b), and 3(c) are SEM images of sprayed, oxidized, and hydrogen reduced coatings. During oxidation, the graphite phase present in the coating layer, and a small fraction of the nickel present in the coating, are oxidized. Hence, the porosity is increased due to the removal of the graphite phase in the form of carbon dioxide. But, as shown in Fig. 3(b), the distribution of pores is not uniform. The oxidation of the smaller nickel particles present in the coating changes the coating structure. The triple phase boundaries on which the oxidation of hydrogen occurs in a SOFC cell are formed by the pores, the YSZ particles, and the nickel. NiO particles in the coating were reduced to Ni particles, and the conductivity of the coating was changed from that of a ceramic insulator to that of a metal conductor. The above process also increases the

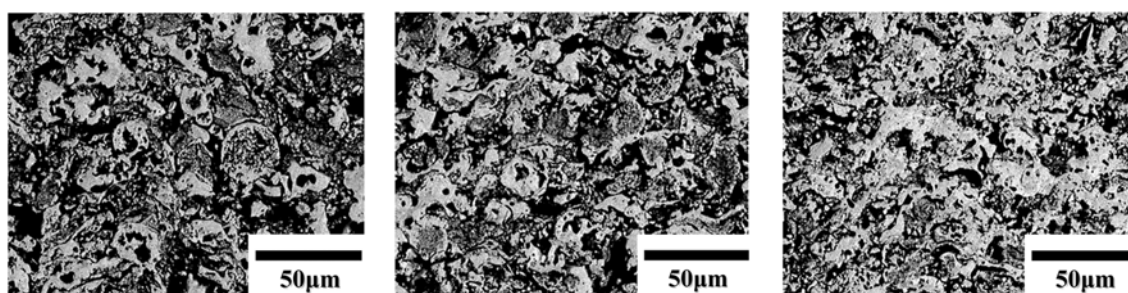


Fig. 2. SEM images of as sprayed NiO/YSZ/Graphite coatings prepared from spray dried powders at different hydrogen flow rates with primary gas; (a) 5 SCFH (b) 10 SCFH and (c) 15 SCFH; 1 SCFH 0.47 = lpm.

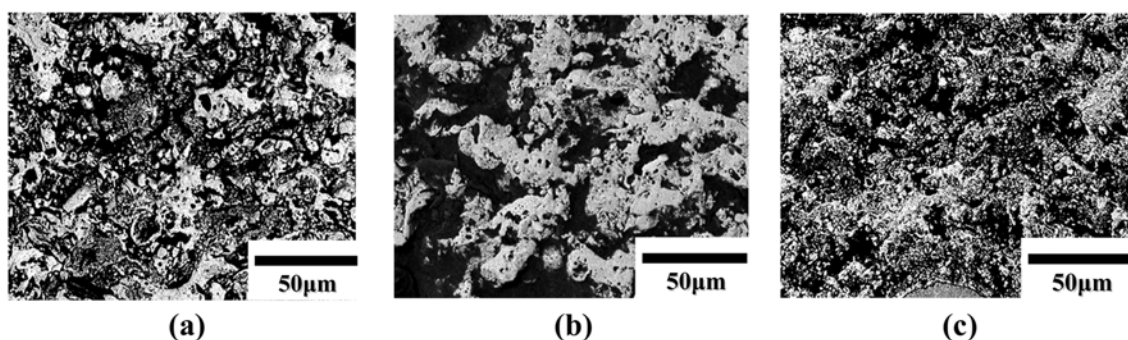


Fig. 3. SEM images of the (a) sprayed (b) oxidized and (c) hydrogen-reduced coatings prepared from spray dried powders.

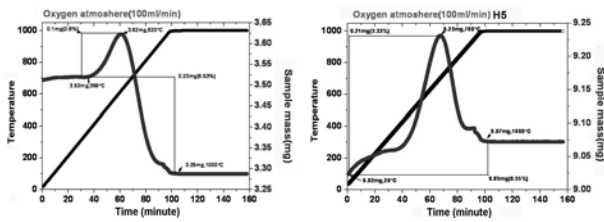


Fig. 4. Thermo gravimetric analysis of (a) feedstock powder and (b) coating prepared at 5 SCFH Hydrogen flow rate.

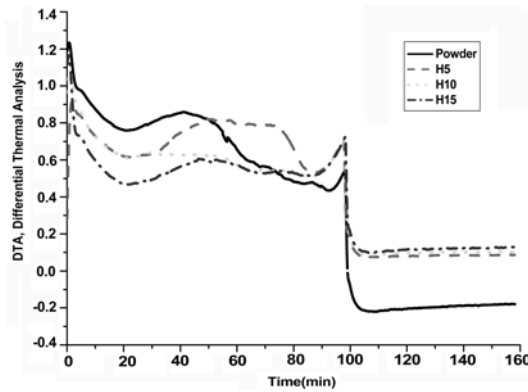


Fig. 5. Differential thermal analysis results of feedstock powder and coatings.

porosity, enabling the flow of gases in the cell. The hydrogen reduction in the coating yields channels through which hydrogen gas can propagate and be oxidized with the oxygen ions coming from the cathode and propagating through the YSZ electrolyte. The YSZ present in the coating forms a conduction network for negative oxygen ions, and Ni forms a conductive network for electrons. During the hydrogen reduction test, the NiO phase present in the coatings was reduced, and the remaining phases were YSZ and Ni. In Fig. 3(c), the white and grey colors in the microstructures indicate YSZ and Ni phases respectively, and the pores (colored black) are uniformly distributed in the coating.

The oxidation and decomposition behavior of the feedstock powder and coatings were studied with TG/DTA analysis. The thermal behavior of the feedstock powder and coatings are shown in Figs. 4 and 5, and in Table 2. Fig. 4 shows the TGA curves of the powders (a) and coatings (b) prepared at the 5 SCFH hydrogen gas flow rate. The weight gain of the powder sample was 2.8% at a temperature range of 368 °C–620 °C, and corresponds to the oxidation behavior of a small fraction of nickel and graphite. This can be seen in the exothermic peak shown in Fig. 5. The weight loss of 9.38% in the temperature range of 620 °C–1,000 °C corresponds to the oxidation behavior of graphite powder present in the feedstock. The 2.8% weight gain corresponds to the oxidation of nickel and the evaporation of graphite powders. Hence, the net weight loss of the feedstock powder sample is 6.53%, as indicated in Table 2. In Fig. 5, the initial decrease is due to the evaporation of the binders and moisture molecules present

Table 2. TGA analysis of the spray dried powder and coating prepared from different secondary gas flow rates

	Change in mass		
	Oxidation (Ni) & Evaporation (Graphite)	Evaporation (Graphite)	Total
Spray dried powder	2.8%	9.38%	6.53%↓
After Coating H5	2.33%	1.77%	0.55%↓
After Coating H10	2.31%	1.96%	0.36%↓
After Coating H15	1.01%	0.93%	0.08%↓

in the samples. Fig. 4(b) shows the thermo-gravimetric analysis of the coating prepared at 5 SCFH hydrogen. The weight gain obtained in the temperature range of 200 °C–700 °C corresponds to the oxidation of nickel and the evaporation of graphite. The weight gain was 2.33%, which is smaller than that of the feedstock powder (2.8%). The weight loss in the temperature range of 700 °C–1,000 °C was only 1.77%. The net weight gain of the coating was 0.55%, which is significantly smaller (6.53%) than that of the feedstock powder. Similar results were obtained for coatings prepared at different hydrogen gas flow rates, and are indicated in Table 2. Increasing the hydrogen gas flow rate during spraying decreases the mass gain. The evaporation of the graphite phase present in the feedstock powder and the coating takes place in two steps, and causes weight losses. The first step occurs with the oxidation of nickel. It is much smaller than that of the same at the higher temperature interval. The powder sample contained a large quantity of the graphite phase. During flight, the fraction of graphite present in the feedstock evaporated prior to deposition. Because the quantity of evaporated graphite is greater, increasing the hydrogen gas flow rate decreased the change in mass. The rate of the evaporation of graphite in the plasma is greater for higher plasma jet temperatures.

Fig. 6(a) shows the Vickers hardness values of the coatings prepared from spray dried powders. The hardness values were measured at eleven locations, and an average was calculated for analysis. For sprayed coatings, the value of the Vickers hardness is higher. It is seen in Fig. 6(a) that the Vickers hardness value decreases for coatings after the oxidation test. During oxidation, the graphite phase present in the coating is oxidized and forms a gas phase

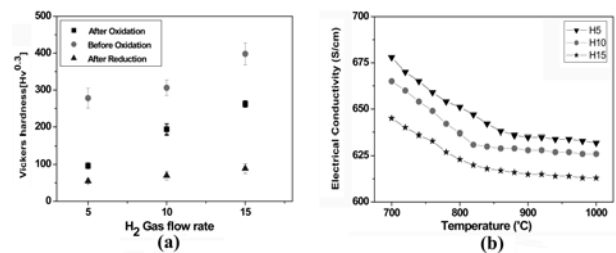


Fig. 6. Vickers hardness value and electrical conductivity of coatings (as sprayed, after oxidized and after hydrogen reduction) as a function of hydrogen gas flow rate prepared from spray dried powders.

oxide, creating porosity. Hence, the Vickers hardness value decreases with the effects of oxidation. The hardness value for coatings prepared at the 5 SCFH hydrogen flow rate is 280 kg/mm². After oxidation, for the same coating the value is decreased to 100 kg/mm².

The Vickers hardness measurements were taken for the same coatings after the oxide reduction test in a hydrogen atmosphere. It is seen in the figure that oxide reduction further decreases the Vickers microhardness values. The NiO phase present in the coatings was reduced in the hydrogen atmosphere, and formed nickel, creating pores in the coating.

Increasing the hydrogen flow rate in the plasma process gas increased the microhardness of the coatings. Hydrogen has a high specific enthalpy, and thus increases the heat flux of the plasma jet. So, with an increased hydrogen flow rate, more heat penetrates the particles and leads to better melting which reduces the porosity. This explains the higher Vickers hardness values associated with the higher hydrogen flow rates. The rate of decline in the Vickers hardness values for the 5 SCFH hydrogen flow rate was greater than that of the higher hydrogen flow rates. Under the 5 SCFH hydrogen flow rate condition, particles were partially melted due to the poor heat flux present in the plasma jet. Hence, during oxidation, many unmolten and partially molten particles may create more pores.

Fig. 6(b) shows the electrical conductivity–temperature graph for the coatings prepared from the spray dried powders. The figure shows that increasing the hydrogen flow rate decreases the electrical conductivity of the coatings. At lower hydrogen flow rates, the fraction of NiO is higher in the coating layer. The magnitude is 620 Siemens/cm at 800 °C. The reference anode shows the lowest electrical conductivity of 160 Siemens/cm at 800 °C [3, 8], which is much lower than the values presented in this studies. The spray drying of powder can provide more triple phase boundaries for the hydrogen oxidation reaction in SOFCs, and is expected to show lower polarization losses in SOFC anode applications.

Also, all of the phases present are very small in size and are in close contact with each other, so there is close contact between the particles in the coating.

Conclusions

Spray coatings were prepared from spray dried YSZ/Ni coatings for application in SOFC anodes. The effects of the particle states in the plasma jet on the properties of the spray coatings were explored through thermal, microstructural, mechanical, and conductivity analysis. The oxidation and decomposition behaviors of the feedstock

powders and spray coatings were studied with TG/DTA analysis. Increasing the hydrogen gas flow rate in the plasma flame decreased the net mass change in the resultant coating as compared to the mass of the feedstock powder. A fraction of graphite present in the feedstock evaporated during the spray process because of high temperatures. Increasing the hydrogen flow rate increased the hardness and decreased the electrical conductivity of the coatings.

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