JTTEE5 15:593-597
DOI: 10.1361/105996306X146811
1059-9630/$19.00 © ASM International

Comparison of Atmospheric Plasma Sprayed Anode Layers for SOFCs Using Different Feedstock

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(Submitted February 20, 2006; in revised form April 26, 2006)

Atmospheric plasma spraying (APS) is a cost-effective way to produce solid oxide fuel cell (SOFC) components. When using APS, therefore, sinter steps can be avoided, which is essential once a metallic support is used for the SOFC. Several properties are required regarding the microstructure of an optimized anode layer. Here, gas permeability, electrochemistry, electronic conductivity, coefficient of thermal expansion, as well as thermal shock resistance have to be considered. Different types of powder feedstock were investigated to develop an atmospheric plasma sprayed anode layer: (a) NiO or Ni together with YSZ as starting materials, (b) agglomerates in which NiO and YSZ are already mixed on a submicrometer range, (c) blended NiO/YSZ powder, and (d) separate injection of the individual NiO and YSZ powders, respectively, into the plasma by two separate powder lines. The performance of APS anodes are measured in single fuel-cell tests. Anode layers sprayed by a separate injection of the individual NiO and YSZ powders into the plasma show the best results.

Keywords cermet coatings, fuel cells, production/preparation technology

1. Introduction

Fuel cells are converting chemical energy directly into electrical energy with low environmental impact. Therefore, fuel cells have to be considered as important energy systems for the future. The high-temperature solid oxide fuel cell (SOFC) shows the maximum electrical efficiency of all types of fuel cells. For SOFC-based systems, the most important issue in becoming a commercial product is the reduction of manufacturing costs. Atmospheric plasma spraying (APS) seems to be an attractive and cost-effective technique for industrial production of SOFCs (Ref 1).

Several requirements must be fulfilled for an anode layer in SOFC systems. The coefficient of thermal expansion has to match that of the other components used. The anode materials must be stable in reducing atmosphere and compatible to the substrate as well as the electrolyte material. A sufficient open porosity is necessary to allow the fuel gas to penetrate through the electrode layer. To guarantee a percolation of the nickel (Ni) and therefore ensure a good electronic conductivity, the Ni content should be above 30 vol.% (Ref 2). Ceramic and metallic phases as well as the pores should be homogeneously distributed over the whole anode layer. A large three-phase boundary (TPB), which is essential for high electrochemical activity, can be obtained by decreasing these domain and pore sizes (Ref 3).

Typically, a Ni/YSZ cermet is used as the anode of SOFCs. Several thermal spray techniques are already being investigated to produce anode layers (flame spraying, Ref 4; vacuum plasma spraying, Ref 5; and APS Ref 6). Usually NiO instead of Ni is used as starting material. The volume change during the reduction of NiO to Ni causes the initial porosity to increase. However, graphite is also being studied as pore former together with Ni/YSZ powder to ensure a sufficient porosity of the anode (Ref 7). Plasma sprayed SOFCs already have shown their great potential with respect to the redox stability of Ni-base anodes as required for auxiliary power units (APU) applications (Ref 8).

In this paper, the powder feedstock to obtain atmospheric plasma sprayed Ni/YSZ anodes is discussed. The most promising powder batches are selected to test the performance of the achieved APS anodes in SOFC operation.

2. Experimental

All plasma sprayed layers were produced using the multicathode Triplex APS torch (Sulzer Metco AG, Wohle, Switzerland) mounted on a six-axis robot. A porous metallic tape-casted and sintered plate based on a ferritic Fe/Cr alloy (Ref 9) was used as substrate. The geometry of this substrate was buttonlike with a diameter of 35 mm and a thickness of about 1.5 mm. To achieve APS coatings, powders were injected perpendicular into the plume carried by an argon gas stream. Fused and crushed powder of 8 mol.% Y_2O_3 fully stabilized ZrO_2 was used to deposit a gastight electrolyte layer by APS (Ref 10). Cathode layers were produced by painting a $(La_{0.6}Sr_{0.4})(Fe_{0.8}Co_{0.2})O_{3-\delta}$ (LSFC) slurry on top of the electrolyte layer.

Particle size distributions were analyzed by Fraunhofer dif-

This article was originally published in *Building on 100 Years of Success, Proceedings of the 2006 International Thermal Spray Conference* (Seattle, WA), May 15-18, 2006, B.R. Marple, M.M. Hyland, Y.-Ch. Lau, R.S. Lima, and J. Voyer, Ed., ASM International, Materials Park, OH, 2006.

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fraction of a 633 nm laser light using the Analysette 22 (Fritsch GmbH, Idar-Oberstein, Germany). The microstructure of the coatings was inspected on cross sections by light microscopy, scanning electron microscopy (SEM), and energy-dispersive microanalysis (EDX). Images of the microstructure were taken using the SEM LEO 1530 (Carl Zeiss SMT AG, Oberkochen, Germany) at 15 kV. To distinguish the different phases, backscatter electron (BSE) images were taken in COMPO mode. The coating porosity is determined by digital image analysis. A perthometer M2 in combination with a probe PFM 6,720,907 (Mahr GmbH, Göttingen, Germany) was used to determine the roughness of the plasma sprayed coatings.

Single fuel cell tests were carried out to determine the electrochemical performance of the SOFC layer system. The reduction of NiO to Ni in the anode electrode occurs during the startup of the SOFC. Voltage versus current density curves were obtained at 800 °C and flow rates of 40 slph (air) on the cathode side and 13.4 slph (H_2) on the anode side, respectively.

3. Results and Discussion

3.1 Powders

To obtain an anode layer by an APS process with a homogeneous mixture of the phases Ni and YSZ and pores, different powder feedstock can be considered. Instead of using Ni powder as starting material, it is also possible to use NiO powder. During the reduction process in the starting phase of the SOFC the anode will gain additional porosity due to the volume change from NiO to Ni.

To end up with a high electrochemical activity of the anode layer, the domain sizes of the components should be in the range of 1 µm or below. On the other hand, due to the flowability, powder particles have to be greater than about 10 µm. Therefore, a mixture of the components has to be already present in the initial powder batch.

3.1.1 Agglomerated NiO/YSZ Powder (NZ-1). The NZ-1 powder is a homogenous mixture of NiO (1153, J.T. Baker, Phillipsburg, NJ) and YSZ (FYT 13-0-002-H, Unitec Ceramics, Stafford, UK) powders, respectively. Both powders are milled to particle size below 1 µm. The powder grains are then coated with a phenol formaldehyde resin as a binder and stuck together, forming agglomerates (Coat mixing). By the CoatMix process (Ref 11) agglomerates of less than 80 µm are formed. In an additional thermal treatment, the powder mix is debindered and sintered to stabilize the agglomerates. This manufacturing method leads to reproducible mixing powders with nearly 100% powder yield.

3.1.2 Powders Containing Metallic Ni. Two powders were studied initially containing Ni instead of NiO: (a) a Ni-coated YSZ (Amperit 992.0, H.C. Starck, Laufenburg, Germany) and (b) a mechanically alloyed (MA) Ni/YSZ. The H.C. Starck powder was a partially 7 wt.% Y_2O_3 stabilized zirconia coated with 30 wt.% Ni. The MA powder was prepared using a high-energy mill (Simoloyer CM01, Zoz, Wenden, Germany). Nickel shows a critical milling behavior; that is, it starts to stick on the grinding media as well as on the milling chamber during the high-energy process. Therefore, the mechanical alloying was performed in a cycled operation, where the rotation speed was alternated between a high and a low value (Ref 12). Even using this cyclic mode, the MA powder output was only poor and an economic powder production was not achievable.

Table 1 Powders selected for SOFC production

	NZ-1	NiO-1	YSZ-1	YSZ-2
Composition	YSZ/NiO	NiO	YSZ	YSZ
Company	FZJ	Harjavalta	Praxair	Sulzer Metco
Route	CoatMix	…	Spray dried	Fused and crushed
Size d_{10}	12 µm	6 µm	17 µm	7 µm
Size d_{90}	40 µm	20 µm	83 µm	23 µm

Both metallic Ni-base powder types showed an uncontrolled partial oxidation of the Ni during the APS process. Additionally, due to the strongly different melting temperatures of Ni (about 1700 °C) and YSZ (about 2700 °C) and the fact of having one metallic and one ceramic component, it is difficult to adjust the parameters for the thermal spray process. Therefore, the coating development using metallic Ni together with YSZ as powder feedstock was stopped after the first APS tests.

3.1.3 Flowable NiO and YSZ Powders. Additional to the powders in which a mixture of the two components were already realized in each particle, flowable NiO and YSZ powders were used directly to optimize the anode layer: NiO-1 (NiO, OGM Harjavalta, Harjavalta, Finland), YSZ-1, a spray dried fully Y_2O_3-stabilized zirconia (ZRO-292, Praxair, Wiggensbach, Germany), and YSZ-2, a fused and crushed powder also fully stabilized manufactured by Sulzer Metco.

3.2 APS Coatings

Powders listed in Table 1 are selected for further optimization of the anode layer by APS. Whereas the NZ-1 powder is already a mixture of the materials NiO and YSZ, the other powders are mixed within the plasma plume (Ref 13). By using the three-cathode APS torch Triplex II, three arcs are formed within the torch. These arcs are relatively stable in position. Therefore, an effective injection of the spraying materials is possible at three different points. Figure 1 illustrates the locally separated injection (SI) of the NiO and YSZ powders perpendicular into the plasma plume. The simultaneous injection of flowable NiO as well as YSZ powders into the plasma flame results in a layer mixed from both components. By optimizing the powder feeding parameters it is possible to obtain anode layers with a homogeneous mixture of the components in the right composition.

The optimized APS parameters for the anode layer production are given in Table 2. The column labeled "SI" is showing the APS parameters used for anodes obtained by a separate injection of two individual powders into the plasma plume.

Due to the rather large particle size of the YSZ-1 powder (d_{10} = 17 µm to d_{90} = 83 µm) the domain size of the YSZ within the SI anode layer are typically above 20 µm. To reduce the YSZ phase size, the YSZ-2 powder with a finer grain size distribution was used for the SI anode production. Micrographs of cross sections of the anode layers obtained by injecting the agglomerated NZ-1 and separately NiO-1/YSZ-2 powder into the plasma plume are shown in Fig. 2. To improve the material contrast between NiO and YSZ, the backscattered electrons of the SEM are detected. The NiO and YSZ domain sizes are in the submicrometer range of the layer achieved using the agglomerated NZ-1 powder. Occasionally, in some splats partial unmolten YSZ particles could be found. The porosity of the layer is clearly

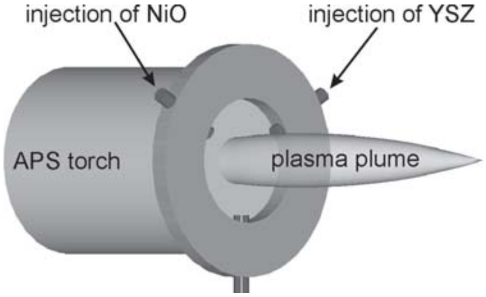

Fig. 1 Separate injection of NiO and YSZ powders into the plasma plume

Table 2 Used APS parameters for anode layer production

	SI anode	NZ-1 anode
Standoff distance, mm	100	150
Ar/He, slpm	25/0	35/0
Discharge current, A	300	350
Powder(s)	NiO-1/YSZ-2	NZ-1
Robot speed, mm/s	500	500
Coating cycles	3	10

dominated by delamination cracks that are typically horizontally arranged. On the other hand, in the anode obtained by a separated injection of the NiO and YSZ powder, respectively, the porosity is mainly dominated by globular pores. NiO and YSZ could be easily distinguished in the micrograph with domain sizes of about 10 µm.

To increase the corrosion lifetime of the metallic substrate used and to allow a sufficient gas supply of the anode layer, the substrate has a coarse structure. In Fig. 2 parts of the metallic substrates are visible. Since the ~40 µm thick electrolyte layer has to be gastight, it is essential to reduce the coarse substrate roughness to moderate values. As shown in Fig. 2, both types of anode layers are able to cover the initially coarse substrate roughness. Hence, the anode layer thickness is not only limited by the capability to have a sufficient electrochemical activity but also by its surface quality.

3.3 SOFC Performance Tests

To carry out electrochemical performance tests, SOFC buttons with a diameter of 35 mm were prepared. The anode as well as the electrolyte layer was deposited by APS. A LSFC slurry was painted on top of the electrolyte layer to provide a cathode. The diameter of the cathode layer is 31 mm centered on top of the electrolyte layer. The measurements were performed on a sealingless SOFC test facility; that is, surplus fuel is burned on the edge of the button cell. The SOFCs were operated at 800 °C using dry H_2 as fuel and air as oxidant. The reduction of the NiO to Ni takes place during the startup of the SOFC. Voltage versus current density curves are measured to determine the electrochemical performance of the developed anode layers. A cross section of such a SOFC layer system is shown in Fig. 3.

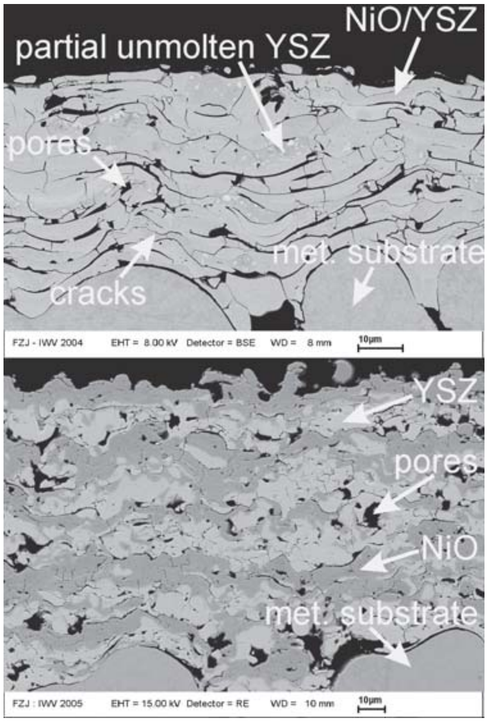

Fig. 2 Cross section of an APS anode coating obtained by (top) using the NZ-1 powder and (bottom) injecting NiO-1 and YSZ-2 powders separately into the plasma plume. SEM image of backscattered electrons

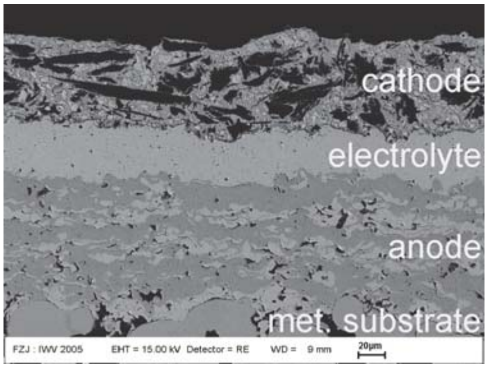

Fig. 3 Cross section of a SOFC layer system in the as-sprayed state. The anode (SI) as well as the electrolyte layer is produced by APS. SEM image of backscattered electrons

SOFC layer systems are prepared having an anode layer based on the agglomerated powder mix of NiO/YSZ as well as by an SI of the individual NiO and YSZ powders into the plasma plume. To compare the capability of the two different anode layer concepts, voltage versus current density curves are given in Fig. 4. The initial performances of the anode using NZ-1 powder and the SI anode using NiO-1 and YSZ-1 powder seem to be comparable. However, one must take into account that contributions regarding the anode layer are probably only secondary effects and are not visible in the V-I curves shown. Nevertheless, the V-I curves of the two anode layer concepts differ from each other after a thermal cycle of the SOFCs from 800 °C to room

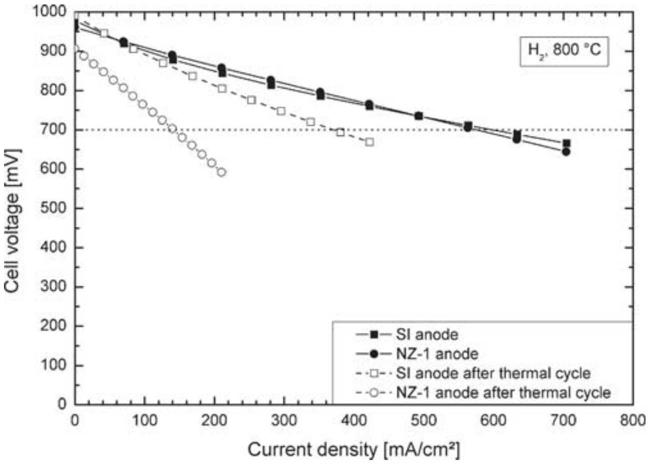

Fig. 4 Voltage versus current density curves of APS sprayed SOFC layer systems before (solid symbols) and after a thermal cycle (open symbols). The anode layers are produced by separate injection (SI) of NiO and YSZ powder (squares) and by injecting NZ-1 powder into the plasma plume (cycles).

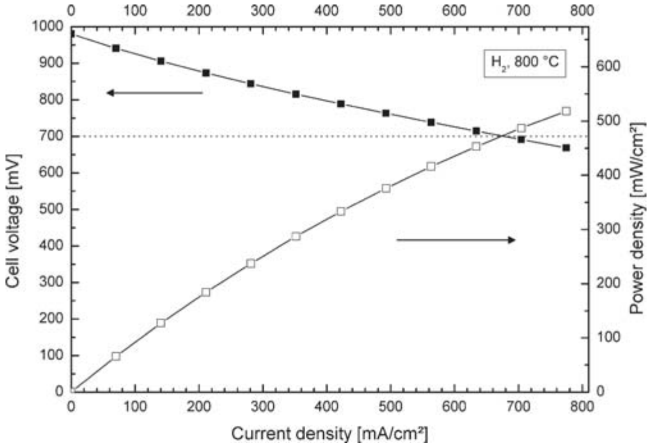

Fig. 5 Cell voltage (solid symbols) and power density (open symbols) versus current density of an APS SOFC layer system. The optimized anode layer is produced by separate injection of NiO-1 and YSZ-2 powder into the plasma plume.

temperature and back to 800 °C. The open-cell voltage of the SI anode remains unchanged after the thermal cycle, and the performance drop can be related to an increase of the area specific resistance. The NZ-1 anode, on the other hand, shows additionally a strong decrease of the open-cell voltage after the thermal cycle. A micrographic inspection of a NZ-1 anode shows that the horizontal delamination cracks already existing in the as-sprayed state (top image Fig. 2) become more pronounced after electrochemical tests. In some cases, vertical segmentation cracks could be found within the electrolyte layer ending inside the anode layer. The horizontal cracks can explain the greater increase of the area-specific resistance, whereas the segmentation cracks inside the electrolyte are probably responsible for the drop of the open-cell voltage.

The large performance loss and the more complicated powder production route of the NZ-1 powder (CoatMix process and an additional debinding/sinter step) are the reasons to focus the further development of the anode on the SI method. The optimized anode layer is shown in Fig. 3. Here the YSZ-2 powder with the smaller particle sizes is used in combination with the NiO-1 powder. Both powders are injected separately into the APS flame to build up the anode layer. A porosity of 9.2 ± 1.3 vol.%, a NiO content of 52 ± 3 vol.%, and a YSZ content of 39 ± 4 vol.% are determined by image analysis on the as-sprayed layer. These values correspond to a metallic Ni volume content slightly above 30% and an open porosity of about 26% in the reduced state of the anode. The electrochemical performance of a SOFC with an optimized anode layer is shown in Fig. 5. At 800 °C and a cell voltage of 0.7 V, a current density of about 675 mA/cm^2 could be drawn, which results in a power density output of almost 500 mW/cm^2. The optimization of the electrolyte as well as the cathode layer is not fully completed yet. Therefore, the cell performance shown here is a snapshot of the development status of plasma sprayed SOFCs. A discussion of the complete, developed SOFC layer system in comparison to plasma sprayed SOFCs from other groups will be published in a separate paper.

4. Summary and Conclusions

To develop an anode layer using the APS process, different concepts were studied, varying the powder feedstock. Ni/YSZ as well as NiO/YSZ powders are investigated. Powders containing metallic Ni are difficult to optimize in combination with YSZ for the APS process. A partial oxidation of the Ni during the spraying and the large difference of the melting temperatures of Ni and YSZ are main reasons to focus on NiO/YSZ powder feedstock. Starting with NiO/YSZ during the deposition process leads to an additional porosity of the anode by reducing the NiO to Ni.

To obtain a large three-phase boundary, a homogeneous mixture of the NiO and YSZ phases is required on a submicrometer range (Ref 3). Therefore, flowable powders are produced already showing these properties within each of the powder particles. Measurements on single SOFCs demonstrate the negligible influence of the phase size on the resulting performance. Thus, SOFCs with an anode layer produced using agglomerated powder mix of NiO/YSZ show almost identical performances to SOFCs obtained from NiO and YSZ powders with larger grain sizes.

Moreover, SOFCs with APS anodes produced by separately injecting (SI) NiO and YSZ powder into the plasma plume have a better thermal cycle resistance. At a cell voltage of 0.7 V and 800 °C, an output of about 500 mW/cm^2 is obtained using this kind of APS SOFCs.

Acknowledgments

This project is funded by the European Union under the “Energy Environment and Sustainable Development (1998-2002)” contract number ENK5-CT-2002-00642 (“CexiCell”). The funding by the EU is gratefully acknowledged. The authors also gratefully acknowledge the work of Dr. V. Haanappel for carrying out electrochemical performance tests, Mr. K.H. Rauwald and Mr. R. Laufs for the manufacturing of the plasma sprayed coatings, Dr. D. Sebold, Mrs. A. Hilgers, Mrs. H. Moitroux, Mr.

D. Weigand, and Mr. M. Kappertz for assistance in sample preparation and characterization.

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