GAS-TIGHT ZIRCONIA ELECTROLYTE LAYERS FOR SOFCs
BY ATMOSPHERIC PLASMA-SPRAYING

R. Vaßen, D. Hathiramani, R. J. Damani
Forschungszentrum Jülich GmbH
Institut für Werkstoffe und Verfahren der Energietechnik (IWV1)
D-52425 Jülich, Germany
1Sulzer Innotec, Sulzer Markets and Technology Ltd.
MAT 1551, P.O. Box 65, CH-8404 Winterthur, Switzerland

ABSTRACT

The major challenge in the development of dense electrolytes by atmospheric plasma-spraying (APS) was the avoidance of cracks typically generated during the spraying process. Compared to conventional plasma-sprayed ceramics both the number of micro-cracks and segmentation cracks have to be reduced considerably to achieve sufficiently low leakage rates. Based on a detailed understanding of the formation of plasma-sprayed coatings, appropriate process conditions have been established to reach the target values. The major influencing factors are the particle properties in the plasma jet, the substrate temperature, the kind of movement of the gun during deposition, the particle size distribution of the used YSZ powder, and the powder feeding rate. In addition, the APS gun plays a major role. With the Triplex II gun it was possible to produce rather thin (≤ 40 µm) YSZ layers with sufficiently low leakage rates without any thermal post-treatment. As substrates, tape-cast ferritic steel sheets have been used. The anode was also sprayed by APS using a separate injection of NiO and YSZ. Electrochemical performance was measured after wet-chemically applying a LSCF cathode. The values of the measured open circuit voltage (OCV) were comparable to the ones of sintered cells, indicating the high density of the produced electrolytes. The optimized cells showed at 0.7 V cell voltage a power density of 500 mW/cm².

INTRODUCTION

Fuel cells can directly convert chemical energy into electrical energy. High efficiencies can be reached also for rather small units which make fuel cells attractive energy conversion systems. High temperature solid oxide fuel cells (SOFCs) show the maximum electrical efficiency of all types of fuel cells. Correspondingly, world-wide efforts exist to introduce SOFCs in different areas of energy conversion covering combined heat and power (CHP) for residential applications (1), distributed energy production (2) or auxiliary power units (APUs) for advanced cars (3). Besides the high degradation rates, a major obstacle which has prevented up to now the wide-spread introduction of SOFC
Based systems into the market are the high production costs of the cells. Different technologies have been investigated in the past including CVD, PVD, wet chemical and thermal spray routes (4, 5, 6, 7). Especially the last two processes have the potential of low cost production due to high deposition rates and the ability to coat large surfaces (8).

All employed deposition techniques have to be able to produce dense coatings of the electrolyte usually made of 8 mol% Y2O3 stabilized zirconia (YSZ). This becomes increasingly difficult for wet chemical methods with subsequent sintering steps if substrates show only reduced or no shrinkage during the co-firing process (“constraint sintering”). Thermal spray techniques do not need shrinkage of the substrates and are hence especially favourable for the coating of substrates with reduced shrinkage as used in cathode supported or metallic substrate concepts.

A prerequisite for the deposition of dense ceramic layers by thermal spray processes is the complete melting of the powder particles during spraying. As YSZ is a material with a high-melting point of about 2700°C in most cases thermal spray processes with high process gas temperatures are used to deposit YSZ. Especially plasma-spraying with gas temperatures above 10000 K is advantageous for this application (9). Plasma-spraying can be performed in a controlled environment, typically at reduced pressures of about 50 mbar, or under atmospheric conditions. The first process is called vacuum plasma spraying (VPS), the second one atmospheric plasma spraying (APS). Since in the VPS process, the plasma gases expand against a reduced low chamber pressure, their velocity is typically larger than in the APS process (10). Correspondingly, the particle velocities are also higher giving typically higher densities. On the other hand, the APS process is considerably cheaper due to shortened processing times and reduced investment costs. However, for both types of deposition processes, a satisfying density of the coatings seems to be difficult to achieve. The reason for these problems is the fact that thermally sprayed coatings of ceramics like YSZ normally form cracks and pores during the spray process and cooling to room temperature (11, 12). Therefore, additional post thermal treatments are frequently necessary to achieve a sufficient gastight layer, like sintering (13), surface treatments by chemical densification (14), or spark plasma sintering (15).

In this paper, it is shown that highly dense YSZ coatings can be produced by an APS process. Essential for the achievement of this goal was an understanding of the formation processes of micro- and segmentation cracks and pores in the ceramic coatings. On this basis specific spray conditions have been developed which largely reduce number and size of the cracks in the coating. The produced YSZ coatings with a thickness below 50 μm are gastight in the as-sprayed condition and no additional thermal treatment is necessary. Single fuel cell measurements demonstrate their functionality as electrolyte layers in SOFC systems.

**EXPERIMENTAL**

The deposition of the atmospheric plasma-sprayed coatings, both anodes as well as electrolyte layers, were made with the three cathode Triplex II APS torch (Sulzer Metco AG, Wohlen) mounted on a six-axis robot. As process gases, argon and helium were used. A porous metallic tape-cast and sintered plate based on a ferritic Fe/Cr alloy (16)
was used as substrate. The geometry of these substrates was button-like with a diameter of 35 mm and a thickness of about 1.5 mm. For the anode coatings, the materials NiO and YSZ were injected as powders separately into the plasma flame. Fused and crushed YSZ powder was used for the manufacture of gastight electrolyte coatings.

The deposition process was optimized by using the in-flight characterization system for particles (DPV 2000 system by Tecnar Automation, Canada) (17). Substrate temperatures were measured using the system 4 M8 pyrometer (Land instruments GmbH, Leverkusen). The leakage rates of the electrolyte layers were calculated from the pressure increase from about 10^{-4} mbar up to air pressure. The measurements have been performed at 5 different locations. The rather high surface roughness of the plasma-sprayed coatings made the sealing of the coatings difficult. As a result sometimes artificially increased leakage rates were observed.

The coatings were characterized by metallographic inspection in optical and scanning electron microscopes (SEM). SEM images were taken using the scanning electron microscope LEO 1530 Gemini (Carl Zeiss SMT AG, Oberkochen) with electron energies of 15 keV. For an increased contrast between YSZ and pores the backscattered electrons were used.

Single fuel cell tests were performed to determine the electrochemical performance of the SOFC layer system. Therefore, a (La,Sr)(Co,Fe)O$_3$ slurry was deposited on top of the electrolyte to operate as an air electrode (cathode). For the so produced cathode layer, no additional thermal treatment was necessary. Sintering of the LSCF cathode layer and the reduction of NiO to Ni in the anode electrode occurred during the startup of the SOFC. Voltage versus current density curves were obtained at 800°C with flow rates of 40 slph air on the cathode side and 13.4 slph dry-H$_2$ on the anode side, respectively.

**RESULTS AND DISCUSSION**

In thermal spray technology, the powder morphology has a major influence on the microstructure of the coatings. Therefore different types of powders have been investigated at the beginning. The results of the leakage rate measurements indicated that fine, fused and crushed powders showed the best performance from all selected powders. For the optimization of the spraying process the particle in-flight diagnostic tool DPV2000 was used. The major process parameters as spraying distance, feeding rate, gun power, composition of the process gases (Ar and He), flow of feeding gas were varied in such a way that a maximum of both velocity and temperature of the particles could be achieved. These velocities were above 300m/s and the temperatures above 3000°C. Compared to particle properties in a conventional APS process, these values are certainly rather high.

In addition to these hot and fast particle parameters, high substrate temperatures above 500°C were chosen. High temperatures were obtained by heating with the plasma torch without additional heating. In the design of the substrate holder, this high thermal loading had to be considered to avoid deformation or overheating of both substrate holder and substrates.
Besides the already mentioned parameters a rather large number of additional influencing parameters control the formation of specific microstructures in the thermal spray process. One of such parameter is the velocity of the gun. This velocity controls the local heating of substrate and coating and plays a major role for the avoidance of substrate deformation and achievement of dense microstructures. With this additional optimization step, the leakage rates of the coatings could be reduced from about 5 - 10 mbar*1/cm²/s for conventionally sprayed YSZ coatings to values of about 0.02 mbar*1/cm²/s. These developments are shown in Fig. 1.

![Figure 1. Improvement of leakage rates of electrolyte coatings.](image1)

In fact, the actual leakage rate of the coatings might be even lower due to two factors. Additional leakages at the outer ceiling of the coatings due to the high roughness values (see Experimental section) increase the leakage rates. Furthermore, rather large defects on the surface of the tape-cast substrates can not be covered by the thin APS coatings. In Fig. 2.

![Figure 2. Micrograph of a tape-cast substrate with a defect coated with an anode and an electrolyte layer.](image2)
A defect with a size of about 100 – 200 μm is shown. Obviously, it is difficult to cover such a defect with an anode and an electrolyte layer each with 50 μm thickness. As a consequence, parallel to the development of the plasma-spraying process the tape-casting of the ferritic steel substrates was optimized to reduce the amount of defects (see Fig. 3). For comparison, pressed stainless steel substrates with a rather ideal surface structure were also coated. These coatings showed leakage values below 0.01 mbar*l/cm²/s.

Figure 3. APS coated tape-cast ferritic steel substrates. While on the left some defects are visible, the right sample shows an improved surface without obvious defects.

A further important result of the present investigation is that it is possible to adjust the coating conditions in such a way that the samples are still flat after deposition. No extended bending of the samples occurred which might be expected due to the high substrate temperatures used. This is achieved by the use of specifically designed substrate holders which can prevent bending during coating deposition and cooling.

Figure 4. Atmospherically plasma-sprayed porous anode and dense electrolyte layer on ferritic steel substrates showing a reduced porosity level of the electrolyte on the right hand side due to further process optimization.

Fig. 4 shows optical micrographs of a metallographic sections of as-sprayed atmospheric plasma-sprayed anode and electrolyte coatings on porous, tape-cast ferritic steel
substrates. In the anode layer the three constituents can be identified: NiO (bright), YSZ (grey) and pores (dark). The bonding of the layer to both substrate and electrolyte appears good, the thickness is about 50 µm.

The electrolyte layer shown in Fig. 4 left reveals only few pores indicating its high density. In the micrograph on the right even these few remaining pores have been eliminated by a further optimization of the APS process.

For a more detailed analysis of the electrolyte microstructure scanning electron microscopy has to be used. Typical SEM micrographs of a metallographic section and of a fracture surface of a densely sprayed coatings are shown in Fig. 5. In this high magnification a few microcracks are visible also in the dense coating. However, size and length of the cracks are much smaller than those found in conventionally sprayed coatings (11). Correspondingly, the fracture surface gives a very compact appearance without the indication of preexisting cracks.

![Figure 5. SEM micrographs of a metallographic section (left) and of a fracture surface (right) of a dense APS YSZ coating.](image)

The presented results could only be obtained because an extended understanding of the formation of ceramic coatings during plasma-spraying was available. For the avoidance of microstructural features as pores and microcracks, the mechanism of their formation has to be known. An outline of these mechanisms and the conditions leading to the formation of these highly dense coatings are given elsewhere (18). A patent has been filed for the process outlined here to obtain dense electrolyte coatings (19).

For the application of the described technology, a transfer to a large substrate geometry as 100*100 mm² is of importance. At present, the manufacture of dense coatings on larger substrates without large deformation of the substrate is under development. First results indicate that the modification of both spraying conditions and substrate holder concept will probably allow the achievement of these targets.

Several cells with APS anode and electrolyte and slurry coated cathodes have been tested with respect to their electrochemical performance. The results are summarized in Fig. 6. The numbers indicate different coating trials in a chronological sequence. Obviously, a
clear improvement of the performance could be achieved. The best cells show open circuit voltages above 950 mV. These values are comparable to the ones found for sintered cells with dense electrolyte. The rather low values compared to the theoretical ones are a result of the used relatively open experimental setup.

The current density data shown in Fig. 6 are calculated by dividing the current by the cathode area. These values give a lower limit for the current density as the current collecting interconnect has a lower area. Using this area would further increase the current densities by a factor of 1.38.

The best cells in Fig. 6 show current densities at a cell voltage of 0.7 V of nearly 700 mA/cm² giving power densities of about 500 mW/cm². As discussed above, these values are lower limits for the actual performance of the cells. The area specific resistances of the best four cells are between 0.4 and 0.6 Ωcm². All the shown results reveal good performance of the optimized cells and the suitability of the APS process for the manufacture of SOFCs.

![Figure 6. Cell voltage and power density of APS cells with slurry coated LSCF cathode as a function of current density. The numbers indicate subsequent coating trials. The data are normalized to an effective area equal to the applied cathode area. Using the current collecting interconnect area increases both current and power density by a factor of 1.38.](image)

**SUMMARY**

Tape-cast ferritic steel substrates have been coated by the APS process with a porous anode and a dense electrolyte. A LSCF cathode was applied by a slurry coating process. It could be demonstrated that with the atmospheric plasma spraying process, it is possible to
produce highly dense YSZ coatings suitable for an application as electrolyte in solid oxide fuel cells. Lower limits of current density of about 700 mA/cm² and power density of 500 W/cm² have been realized. This technological breakthrough has been achieved by optimizing “hot” spraying conditions towards micro-crack free coating deposition.

ACKNOWLEDGMENTS

The majority of the presented results were obtained within the project “Cexicell”. The funding of this project by the European Union under the “Energy Environment and Sustainable Development (1998-2002)" contract number ENK5-CT-2002-00642 (“CexiCell”) is gratefully acknowledged. The authors also gratefully acknowledge the manufacture of the plasma-sprayed coatings by Mr. K.H. Rauwald and Mr. R. Laufs, and the characterization of the samples by photography, SEM, XRD, and optical microscopy by Mrs. A. Hilgers, Mrs S. Schwartz-Lückge, Mrs. H. Moitroux, Dr. D. Sebold, Mr. P. Lersch, Mr. D. Weigand, and Mr. M. Kappertz (all from IWV/FZ Jülich GmbH). Special thanks also to Dr. H.P. Buchkremer and J.-E. Döring for their advice.

REFERENCES

1. H. Raak, R. Diethelm, S. Riggenbach, in Proceeding of the Fifth European Fuel Cell Forum Proceedings, Joep Huijsmans, Editor, p. 425, European Fuel Cell Forum, Lucerne, Switzerland, (2002).
2. T. Flower, in The Fuel Cell World Proceedings, Ulf Bossel, Editor, p. 258, The Fuel Cell World, Lucerne, Switzerland, (2004).
3. J. Zizelman, C. DeMinco, S. Mukerjee, J. Tachtler, J. Kammerer, P. Lamp, in The Fuel Cell World Proceedings, Marcus Nurdin, Editor, p. 306, The Fuel Cell World, Lucerne, Switzerland, (2002).
4. R. Henne, E. Fendler, M. Lang, in First European Solid Oxide Fuel Cell Forum Proceedings, U. Bossel, Editor, p. 617, European Fuel Cell Forum, Baden, Switzerland, (1994).
5. Y. Ohno, Y. Kaga, S. Nagata, Trans. Inst. Electr. Eng. Jpn., 107, 59 (1987).
6. R. Zheng et al., J. Chin. Ceram. Soc., 31, 598 (2003).
7. G. Schiller, R. Henne, M. Lang, M. Müller, Mater. Sci. Forum, 426-432, 2539 (2003).
8. K. Okumura, Y. Aihara, S. Ito, S. Kawasaki, Journal of Thermal Spray Technology, 9(3), 354 (2000).
9. P. Fauchais, A. Vardelle, B. Dussoubs, Thermal Spray 2001, p.1, C. C. Berndt, K. A. Khor, E. F. Lugscheider, Editors, ASM International, Materials Park, OH, (2001).
10. E. Fendler, R. Henne, M. Lang, in Proceedings of the 8th International Thermal Spray Conference, p. 533, Houston, Texas.
11. R. Vaßen, F. Träger, D. Stöver, J. Therm. Spray Technol., 13(3), 396-404 (2004).
12. H. Zhang, W. Wang, G. Wang, , *IEEE Conf. Record of 30th Int. Conf. on Plasma Science*, p. 361 (2003).

13. Y. Aihara, S. Ito, S. Kawasaki, in *SOFC-IV*, M. Dokiya, O. Yamamoto, H. Tagawa and S. C. Singhal, Editors, *PV95-1*, p. 180, The Electrochemical Society Proceedings Series, Pennington, NJ, (1995).

14. T. Okuo, Y. Kaga, A. Momma, *Denki Kagaku*, 64, 555 (1996).

15. K. A. Khor, L.-G. Yu, S. H. Chan, X. J. Chen., *J. Eur. Ceram. Soc.*, 23, 1855 (2003).

16. Crofer 22 APU, Material Data Sheet No. 8005, ThyssenKrupp VDM GmbH, Germany.

17. J.-E. Döring, R. Vaßen, D. Stöver, in *Proceedings of the Intern. Thermal Spray Conference ITSC*, p. 440 (2002).

18. R. Vaßen, D. Hathiramani, D. Stöver, to be published in *Proc. of the International Thermal Spray Conference*, Bael, Switzerland, 2005.

19. German patent application, filed 13.9.2004