

# PLASMA SPRAYING OF POROUS Ni/ZrO<sub>2</sub>-CERMET ANODES FOR THE SOLID OXIDE FUEL CELLS

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## Introduction

Fuel cells convert the reaction energy of gaseous fuels directly into electrical energy. In the case of solid oxide fuel cells (SOFC) the reaction educts and products are transported to and removed from the electrode/electrolyte interfaces through the porous electrodes. The gas-tight electrolyte consisting of Yttria Stabilized Zirconia (YSZ) with an ionic conductivity separates the electrodes. The materials conventionally used for the anode and the cathode are a Ni/YSZ-cermet and a La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM), respectively. Therefore the multilayer structure Positive electrode - Electrolyte - Negative electrode (PEN) consists of ceramic and metallic components in dense and porous manner.

Vacuum plasma spraying (VPS) promises a great potential to meet the economic requirements as well as the demanded technical specifications of the PEN production. Compared with conventional production processes the number of production steps and the production time can be reduced if the whole PEN was manufactured by VPS in a consecutive spray process. Furthermore, application of thermal spray methods avoids reactions between the cathode and electrolyte during the manufacturing due to the rapid and independent solidification of each particle on the substrate surface. Using conventional shaping plus sintering processes for PEN fabrication undesired phases may occur at the cathode/electrolyte interface. Another advantage of the VPS process is the possibility to build up layers with graded composition and porosity

Thermal spray methods have been studied for already 30 years for the production of SOFC components. Recently, Japanese, American and European groups are working on the integrated production of the PEN. By performing VPS experiments Yoshida et al. found that successive spraying of the PEN is manageable (1). Actually, all components of a PEN element for a Heat Exchanger Integrated System (HEXIS) can be manufactured by VPS (2). Additionally, the application of Laval torch nozzles further reduces the particle's residence time in the plasma jet, thus allowing thermally instable materials to be sprayed. The high velocity and laminarity of the plasma jet enables the production of very dense layers. Furthermore high deposition rates can be obtained with these nozzles (3).

This work is focused on the production of porous electrodes. An optimum mixing of the Ni and YSZ phases of the anode and a good physical contact between both materials is required to achieve a high electrochemical performance as well as a sufficient mechanical stability and reliability. Furthermore an extended Ni - YSZ - fuel gas three phase boundary is of special interest to guarantee high oxidation rates of fuel gas what directly increases the efficiency of power generation by SOFCs. Additionally, the microstructure of the electrode layers must be adapted with respect to the long term stability. The aim of the present work is to optimize the starting material, the VPS equipment and process according to the requirements of the production of a porous anode for SOFCs.

## Materials and Experimental Procedure

A mixed Ni/YSZ (70/30 wt.%) as well as separately injected NiAl and YSZ powders were used for the plasma spray experiments. The powders were specially adapted for the VPS technique. Both, the NiAl and the Ni/YSZ powders were agglomerated (Fig. 1). The grain or the agglomerate distributions of the powders are shown in Fig.2. The mean grain or agglomerate sizes for the YSZ, the Ni/YSZ and the NiAl powders are 12, 30 and 40  $\mu\text{m}$ , respectively.

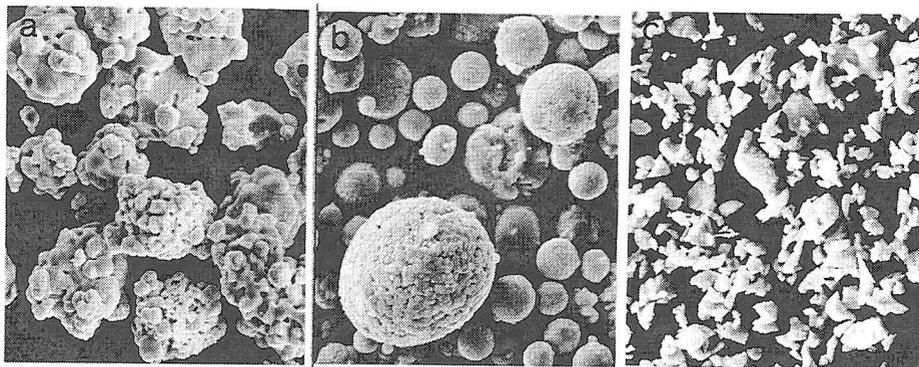


Fig. 1 - Morphologies of the used spray powders a) Ni/YSZ, b) NiAL and c) YSZ.

Two principle approaches were carried out to produce anode layers with a sufficient porosity. Firstly, the mixed Ni/YSZ powder was used. Secondly, the NiAl and YSZ powders were separately fed during the plasma spray process and deposited together on the substrate. Subsequently, the Al was etched out of the layer with a 25% KOH solution enriched with 10% Na-K tartrate.

The coatings were deposited on Ni and YSZ substrates. Their surfaces were sand-blasted and etched with HF, respectively. The YSZ substrates were preheated with the plasma jet prior to the deposition process in order to avoid cracking due to thermal stresses.

Three types of torch nozzles were used for the experiments: (i) a Mach 3 Laval-nozzle with a notch diameter of 6 mm (ii) a modified Mach 3 Laval-nozzle with a notch diameter of 7 mm and (iii) a commercially available standard nozzle adapted to a chamber pressure of 20-200 mbar. The VPS parameters i.e. torch power, plasma gas composition and flow rate, chamber pressure and spray distance were varied as summarized in Table I in order to obtain layers with open porosity. The Ni/YSZ content must be adjusted by the variation of spray parameters.

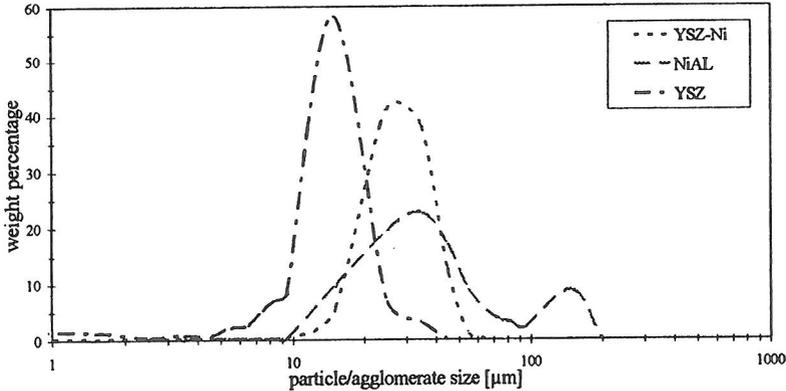


Fig. 2.- Particle/agglomerate size distribution of the used spray powders.

The microstructure of the deposits was studied by light microscopy and SEM. The phase stability, the crystallinity and the phase content of the as-sprayed layers were examined by X-ray diffraction measurements and microprobe analysis. Porosity measurements were carried out on some Ni/YSZ layers by an image analysing system. The electrical resistance of the plasma-sprayed anodes was determined with the four point probe method up to 1200°C.

Tab. I Plasma spray parameters

Powder	Ni/YSZ	Ni + YSZ
Plasma gas [SLpM]	25-45 Ar, 0-50 He, 0-4 H <sub>2</sub>	35-40 Ar, 0-20 He, 0-6 H <sub>2</sub>
Torch power [kW]	19-35	20-30
Chamber pressure [mbar]	80-300	100-200
Spray distance [mm]	16-37	15-30

## Results and Discussion

A specific problem of the production of porous Ni/YSZ layers by VPS is the simultaneous deposition of two materials with a different melting behaviour VPS conditions must be found under which the surfaces of the YSZ particles are just in a

molten state at impact and the Ni particles are neither thoroughly molten nor already evaporated. The development of controlled porous anodes based firstly on the variation of the parameters of the VPS method. Especially the influence of different plasma torch nozzles was studied. With the standard nozzles the layers revealed more porous compared to those made by nozzles with Laval-contour because of the lower plasma jet velocity. However, the investigations showed that in principle it is possible to produce layers with the same porosity with the Laval-nozzles if some adaptations are made. The notch diameter of the nozzle was increased in order to broaden the plasma plume what reduces the plasma velocity. The porosity of the Ni/YSZ layers which was produced with the modified nozzle is between the porosity of those layers which were produced with the conventional and with the unmodified Laval-nozzle [Fig.3]. The deposition rate of the plasma spray process using the modified Laval-nozzle is also between those using the conventional and the unmodified Laval-nozzle. However, the ratio of the YSZ- to the Ni-content which should be about 70/30 Vol.% is the highest in layers produced with the modified Laval-nozzle. This can be explained by the melting rate of the YSZ. For the next step of parameter optimization the effect of plasma gas was examined. The addition of H<sub>2</sub> results in a higher heat conductivity and a lower viscosity of the plasma compared to a pure Ar plasma. Also an Ar/H<sub>2</sub> plasma has an increased plasma enthalpy what improves the melting conditions of the powder particles. The anode layers produced by VPS with Ar and H<sub>2</sub> as plasma gas show low porosity and high YSZ contents. The addition of He has two contradictory effects: (i) it increases the plasma gas viscosity and decreases the velocity of the plasma jet, (ii) the higher plasma viscosity with raised momentum transfer can increase the particle velocity. However,

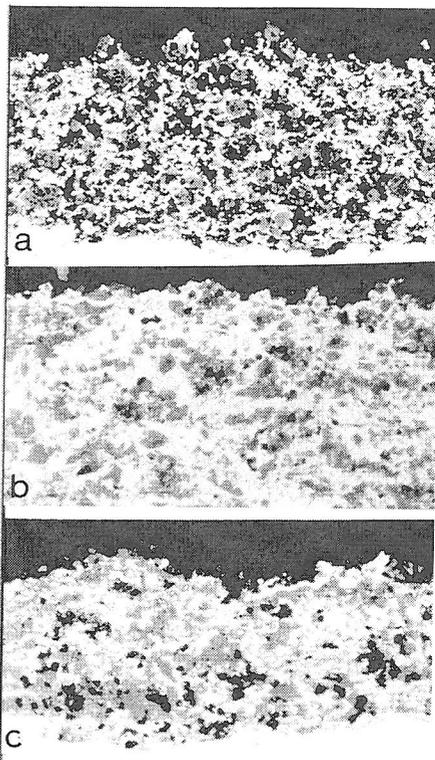


Fig. 3 - Cross section of Ni/YSZ layers deposited with different plasma torch nozzles: a) standard nozzle, b) Laval-nozzle (notch diameter: 6mm), c) modified Laval-nozzle (notch diameter: 7mm). Plasma spray parameters: plasma gas: 38 SLpM Ar, 20 SLpM He, 4 SLpM H<sub>2</sub>; plasma power: 30 kW; chamber pressure: 200 mbar; spray distance: 220 mm (black: pores, grey: YSZ, white: Ni).

with the applied parameters and nozzle configuration higher deposition rates and layers with increased porosity and YSZ contents were achieved using a plasma consisting of Ar, H<sub>2</sub> and He.

The parameter studies showed that a gun power of at least 25 kW is necessary to melt the YSZ particles at all. In this case the content of YSZ in the deposite is very low what results in dense layers due to the high Ni content. However, increasing the power to more than 30 kW also results in Ni/YSZ layers with low porosity due to the completely molten YSZ droplets during the plasma spray procedure (Fig. 4).

To attain a high porosity the chamber pressure and the spray distance must be increased compared with the parameters for dense layers in order to diminish the velocity and the melting degree of the particles at impact on the substrate surface. The ratio of chamber pressure and layer porosity, YSZ content and depositon rate shows a maximum. The optimum chamber pressure for a modified Laval nozzle and for the use of optimized plasma parameters (plasma

gases: Ar, He and H<sub>2</sub>; plasma power: 30 kW) was found to be 200 mbar. Figure 3c depicts an anode layer produced with optimized plasma spray parameters. The electrical resistance was measured on such layers. At operation temperature (950 °C) the electrical resistance is  $7 \cdot 10^{-6} \Omega$  what is about five times less than comparable values from literature (4). This can be explained by the lamellar microstructure of the particles in the Ni/YSZ layer which is typical for plasma-sprayed deposits.

The co-deposition of NiAl and YSZ powder and a subsequently etching out of the Al lead to a very fine microstructure as it is to be seen in Fig. 5. With the separate feeding of the two powders it is also possible to obtain graded layers. First experiments on this subject were successful. Another advantage of the separate feeding is that the requirements of the different powders of the deposition parameters can be met due to the property of the equipment to feed the powders at different ports within the nozzle. The YSZ powder injection was placed on the hottest injection zone of the torch nozzle and the NiAl or Ni powder were placed further downstreams or even outside the

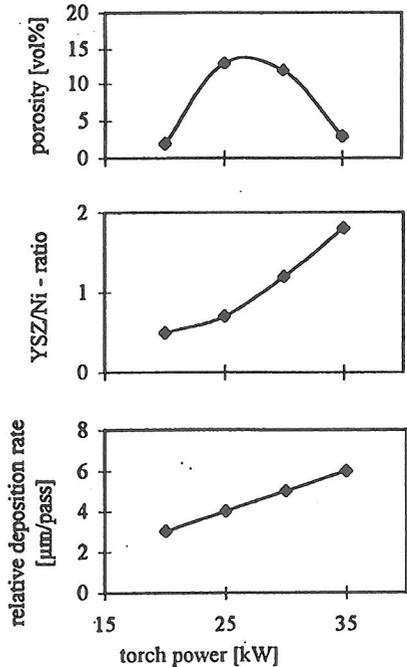


Fig. 4 - Influence of torch power on Ni/YSZ layer characteristic.

nozzle. With this arrangements the YSZ content as well as the porosity in the plasma-sprayed anode layers could be further increased.

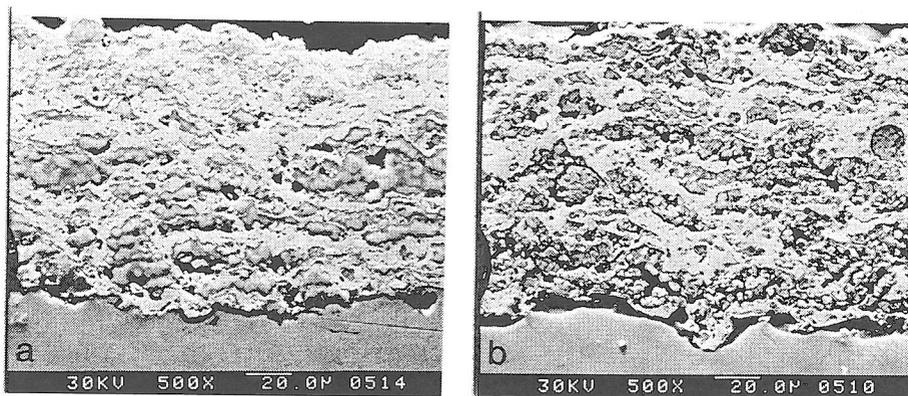


Fig. 5 - As-sprayed (a) and etched (b) NiAl-YSZ layer (white: YSZ, grey: Al, dark: Ni, black: pores).

## Conclusion and Outview

The VPS method was used to produce porous Ni/YSZ cermet layers as anode for an SOFC. The deposition of porous Ni/YSZ cermets demanded a modification of the Laval-nozzle. With this modification high deposition rates compared to conventional nozzles could be attained. The deposition of NiAl-YSZ and subsequent leaching of the Al is a successful method to produce anode layers with very fine porosity.

Up to now the feasibility of producing porous deposits was examined. The next step of investigation will be the electrochemical testing of the electrodes. The results of those tests will influence the further development of the anode's and cathode's microstructure.

## References

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