DEVELOPMENT OF PLASMA SPRAYED COMPONENTS FOR A NEW SOFC DESIGN

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ABSTRACT

The vacuum plasma spraying technique has been further developed and adapted to manufacture the central multilayer MEA component in one consecutive spray process. This enables a new SOFC design with a supporting porous substrate, porous electrode layers with graded composition and porosity and a thin, dense electrolyte layer. The features and specific properties of the vacuum plasma spray process and the adaptation of the SOFC design corresponding to the production method are reported. The state of the development of plasma sprayed MEA layers and of the entire multilayer MEA compound are presented.

INTRODUCTION

A basic requirement for a future widespread application of solid oxide fuel cells is the availability of economical production methods which are also suited for series production. At present, the central SOFC component, the membrane-electrode-assembly (MEA), is fabricated by time-consuming sinter methods which include tape-casting and sintering of the yttria-stabilized zirconia (YSZ) electrolyte and screen-printing and co-firing of the porous electrodes consisting of perovskite-type (La,Sr)MnO₃ and a YSZ/Ni cermet, respectively (1). Sinter processes take relatively long production time and problems due to thermal stresses and material shrinkage may occur. Also, the preparation of electrode layers graded with respect to composition and porosity is not easy to be produced by such processes. In general, the demands which are made on the different layers of the MEA are as follows: (i) high purity electrolyte layers with high ion conductivity and high gastightness with the least possible thickness, (ii) graded controlled porous cathode layers consisting of perovskite-type oxides, (iii) Ni/YSZ cermet anode layers with graded composition and porosity.

A production method which fulfills the technical requirements of processing both metals and ceramics to dense or controlled porous layers resp. to multilayer arrangements and having also the potential of cost reduction in a future series
production is the vacuum plasma spraying (VPS) technique (2,3). At the DLR Stuttgart the VPS process has been further developed and adapted to the specific requirements of SOFC components manufacturing. The utilization of plasma torches with specially developed Laval-like nozzles enables the simultaneous processing of spray powders with very different properties (4). By applying appropriate nozzles and special spray parameters it is possible to produce very dense layers for the electrolyte as well as porous layers for the electrodes with graded composition and porosity in the transition regions. Furthermore, the VPS technique offers the possibility to manufacture the entire multilayer MEA in one fast consecutive process. This may reduce considerably the number of production steps and hence production time compared to conventional sinter methods and thus promising substantially reduced costs especially if less expensive spray materials can be used. However, the production of the entire MEA by vacuum plasma spraying also requires a modified cell design which is adapted to the characteristics of the VPS process. The present paper reports about the features and specific properties of the VPS process, the adaptation of the SOFC design corresponding to the production method and the state of development of plasma sprayed cell components and cells at the DLR.

VPS-ADAPTED MEA DESIGN

The manufacture of the whole electrolyte-electrodes multilayer arrangement by vacuum plasma spraying in one consecutive process simplifies the production process and may lead to lower production costs. The application of this technique, however, demands modifications in the SOFC design. The principle of a new design adapted to the requirements of a totally plasma sprayed cell is shown in Fig. 1 in a schematic drawing. The plasma spray technique requires a substrate to be coated. To ensure the transport of the fuel gas to the three-phase boundaries in the anode the substrate has to consist of a porous material such as for instance a nickel net or felt. The first layer is the YSZ/Ni cermet anode; a gradually reduced nickel content towards the electrolyte layer diminishes the stresses resulting from the mismatch of the thermal expansion coefficients of Ni and ZrO₂. Additionally to the grading in composition also a grading in porosity should be beneficial for the anode layer. A coarse porosity guarantees the gas transport and is advantageous for the long-term stability of the electrode structure. However, close to the anode/electrolyte interface a fine dispersed pore distribution is required to increase the amount of three-phase boundaries where the electrochemical reaction takes place. By means of vacuum plasma spraying it is in principle possible to realize such a graded idealized electrode structure.

Due to the use of a substrate in a VPS adapted MEA design the electrolyte layer has no longer to be the mecanically supporting part. Hence, it can be made thinner resulting in reduced ohmic losses and also in material consumption. The objective in the optimization of the electrolyte layer is to decrease the thickness to a minimum.
which is given by the necessity to be sufficiently gastight. A thickness of about 30 µm for a dense gastight electrolyte layer is a reasonable value which can be achieved by VPS. The structure of the transition to the cathode layer and the cathode itself is of special interest for the performance and efficiency of the cell since the highest voltage losses are probably caused by the oxygen reduction process. An optimized cathode should consist of a dense and thin transition layer followed by a porous electrode layer. The dense cathode region is supposed to exhibit a higher electrical and ion conductivity whereas the porous layer provides extended three-phase boundaries for the electrochemical reduction process. With vacuum plasma spraying a graded transition from a dense to a porous layer can also be realized in the case of the cathode.

EXPERIMENTAL

The method of vacuum plasma spraying and the equipment used at the DLR Stuttgart have been described in detail elsewhere (5,6). Here, only a short description of the special features of the DLR installation which are essential for the production of SOFC components is given.

The equipment is based on commercially available components (Plasmatechnik AG/Sulzer-Metco, Wohlen, Switzerland), but essential parts have been developed in-house to adapt the spray process to the requirements of components to be produced for electrochemical applications. The modifications are related especially to the plasma torch and the nozzle. In order to generate a long and laminar plasma jet, nozzles with Laval-like contours designed for supersonic plasma jet velocities have been developed and investigated by analytical methods (7,8). Laval nozzles have been added to a standard APS (atmospheric plasma spraying) torch but also novel plasma torches where the Laval nozzle contour is integrated within the anode of the plasma torch have been developed and applied. With these torches plasma jet velocities of up to 3000 m/s and spray particle velocities exceeding 800 m/s can be achieved. Laser Doppler anemometry (LDA) measurements revealed that the spray material passes close and parallel to the jet axis resulting in favourable melting conditions. Another feature of the plasma torches used is the internal powder injection by several integrated powder injection ports which are arranged at different positions along the nozzle. Depending on the melting properties of the powders to be sprayed injection ports at different locations have to be used. This arrangement allows also spraying of very different materials simultaneously. By applying optimized spray parameters with appropriate torches and nozzles complex coatings, such as graded cermet layers, exhibiting a desired material and porosity profile can be realized. Furthermore, the powder injection ports can also be used for feeding additional gases into the plasma resulting in plasmachemical effects. The processing of thermally sensitive oxides by VPS is essentially based on the development of this “reactive plasma spraying“ process (9).
Specially adapted spray powders were used for the deposition of the MEA layers by the VPS technique. Ni powder (Metco Westbury, NY, USA) with a grain size \(-45 \mu m\) was used for the nickel interlayer on the nickel substrates. For the production of the anode layers different approaches were developed using the following powders: (i) mixed Ni/YSZ (30/70 wt.\%) powder \((-45 + 10 \mu m, \text{Medicoat, Niederrohrdorf, Switzerland})\), processed together, (ii) separately fed Ni powder \((-45 \mu m, \text{Metco, Westbury, NY, USA})\) or NiAl (50/50 wt.\%) powder \((-44 \mu m, \text{H. C. Starck, Berlin, Germany})\) or NiO powder \((-25 + 10 \mu m\) and \(-44 + 10 \mu m\) resp., Cerac, Milwaukee, WI, USA) and YSZ (11.6 wt.\% \text{Y}_2\text{O}_3) powder \((-22 + 10 \mu m, \text{Medicoat, Niederrohrdorf, Switzerland})\). The same YSZ powder was also used for spraying the electrolyte layer. The spray powder for the cathode layer had the composition \text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 (\text{Medicoat, Niederrohrdorf, Switzerland})\) with a grain size \(-63 + 10 \mu m\). The parameter optimization for the different powders were carried out with different plasma gas compositions (Ar, Ar + He, Ar + \text{H}_2), torch power (14 - 30 kW), chamber pressure (8 - 30 \cdot 10^3 \text{ Pa}) and spray distance (150 - 370 mm).

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 and X-ray microprobe analysis. Porosity measurements were carried out by image analysis, gas adsorption and Hg porosimetry.

RESULTS AND DISCUSSION

Development of Plasma Sprayed MEA Components

A promising step towards simplification and increased economical production of the MEA is expected from manufacturing the entire MEA compound by vacuum plasma spraying in one consecutive process. With this objective, it is obvious to develop the various layers of the MEA arrangement at first separately in order to establish the optimum spray parameters for the very different deposition processes. Accordingly, the results of the plasma sprayed anode, electrolyte and cathode layers are given first, followed by first results of vacuum plasma sprayed multilayers in the course to an entirely plasma sprayed MEA.

Electrolyte. For different applications various Laval nozzles for different plasma jet velocities in the Mach number range between 2 and 5 have been developed. Applying the nozzle contours of the DLR torches with the controlled expansion of the plasma higher plasma jet velocities can be achieved compared to jets of standard nozzles. The higher plasma jet velocities result also in higher spray particle velocities which means high kinetic energy for the particles at substrate impact. Additionally, the radial temperature and velocity gradients are smaller and the jet core with high temperature and velocity values is more extended with such nozzles resulting in good
melting conditions for a higher amount of particles. These advantages lead to denser coatings and more homogeneous layers with high deposition rates. Fig. 2 shows a metallographic cross section of such a dense VPS-YSZ electrolyte layer exhibiting very low porosity. Thus, dense and gastight layers by processing high melting YSZ spray material with vacuum plasma spraying are available even with thin layers of about 30 μm thickness. The use of different grain sizes has a remarkable influence on layer properties. The densest layers were obtained with fine-grained powders. The plasma spray parameters for these powders were optimized by means of Laser Doppler anemometry measurements which allow the determination of the velocity and the distribution of the particles in the plasma jet. Especially the adaptation of plasma gas composition and powder carrier feed rate was necessary to get the fine-grained powder in the hot zone of the plasma jet.

Anode. A specific problem of the production of porous Ni/YSZ layers by VPS is the simultaneous deposition of two materials with very different melting properties. The interior powder injection and the almost central and axis parallel conduction of the spray particles in the long plasma jets provide an optimum environment for a sufficient melting of the spray material. The different powders have to be injected at different locations in the nozzle according to different temperature zones in the plasma. When using a mixed powder spray conditions have to be applied where the surface of the YSZ particles are just in the molten state at impact and the Ni particles are not already evaporated. The layer porosity can be controlled by the proper selection of the plasma torch nozzles and the spray parameters. If porous, but nevertheless well bonded layers are required, a “slower“ nozzle with smaller aperture ratio or enlarged notch diameter has to be used. Additional options to produce porous coatings are the reduction of jet and particle velocity by raising the tank pressure, increasing the spray distance resulting in less flattened particle splats and also in voids, the use of coarser spray powders and/or reduction of torch power. Then, the particles are not fully melted and their deformation at impact is diminished. Optimized plasma spray parameters using a modified Laval nozzle were established to produce porous anode layers from premixed YSZ/Ni powder with the ratio 70/30 wt.%. With separate feeding of the two powders it is possible to obtain graded anode layers which is shown in Fig. 3. Image analysis of the layer cross sections revealed a porosity of approximately 15 vol.%. Enhanced porosities can be obtained by using YSZ + NiO and YSZ + NiAl powders. After the reduction of NiO to Ni at the operating temperature of the SOFC with H₂ a porosity of up to 28 vol.% and a mean pore size of about 200 nm could be measured by Hg porosimetry. A very fine microstructure of cermet anode layers can also be produced by co-deposition of NiAl and YSZ powder and subsequent leaching of the Al content. Porosimetry measurement by gas adsorption revealed a specific surface area of 12 m²/g.

Cathode. For the production of porous cathode layers the same measures with respect to torch nozzles and spray parameters can be taken as already described.
for the preparation of porous anodes. The selection of powder grain size is limited due to the production process of the perovskite powder. Hence, the adaptation of the spray parameters - decreased torch power, increased pressure and spray distance - is the key for porous layers in this case. An additional problem in the case of perovskite powders is their tendency for decomposition. The special Laval nozzles used at the DLR exhibit favourable properties in order to avoid or suppress decomposition of thermally sensitive oxides. A reduced central peak temperature and a broadened temperature profile of these nozzles resulting in improved melting conditions for the spray powders enables the reduction of torch power and hence of thermal load. Additionally, plasmachemical effects can be applied to stabilize thermally sensitive oxides by feeding the powder with oxygen into an enthalpy rich plasma with moderate temperature (Ar + He mixture as plasma gas). Fig. 4 shows a SEM micrograph of an optimized porous La_{0.8}Sr_{0.2}MnO_3 (LSM) layer. XRD analysis proved that almost no decomposition of the perovskite phase occurs during plasma spraying of LSM powder.

**Development of Plasma Sprayed Half Cells and Cells**

The first approach for plasma sprayed cell components was the deposition of Ni/YSZ anode layers onto sintered YSZ electrolyte plates with a thickness of 1 mm and 0.65 mm, respectively. Different spray powders (agglomerated YSZ - 30 wt.% Ni, YSZ + Ni, YSZ + NiAl, YSZ + NiO) were used to fabricate anode layers with different microstructures; screen printed layers of La_{0.8}Sr_{0.2}MnO_3 were applied as cathodes. The YSZ - (LaSr)MnO_3 half cells were preheated up to 600 °C prior to the deposition process in order to avoid cracking due to thermal stresses. The comparison of the electrochemical cell performance of the plasma sprayed anodes and of a screen printed anode (Siemens AG, Germany) with the same electrolyte thickness showed very similar characteristics when agglomerated YSZ - 30 wt.% Ni and YSZ + Ni spray powders were used. The electrochemical measurements proved a comparable behaviour for plasma sprayed and screen printed anodes under identical conditions. Details about these investigations are given in the paper "Production and characterization of vacuum plasma sprayed anodes for solid oxide fuel cells" in this proceedings volume.

The next step in the development of the entirely sprayed SOFC was the production of plasma sprayed anode/electrolyte half cells onto a nickel felt substrate which is shown in Fig. 5. The first layer is a graded Ni/YSZ cermet anode layer with increasing YSZ content towards the electrolyte layer. The anode was produced by separate injection of Ni and YSZ powders at different locations along the torch nozzle resulting in good grading of Ni (light) and YSZ (grey) phases. The top coating of the YSZ electrolyte which completes the half cell arrangement is dense with a thickness of about 80 μm. Recently, also an entirely plasma sprayed MEA consisting of the anode, electrolyte and cathode layer on a Ni felt was fabricated. The metallographic cross
section of the VPS multilayer arrangement (Fig. 6) shows the three layers with desired microstructure and porosity deposited on a nickel felt substrate. The anode, electrolyte and cathode layers have a thickness of 80 μm, 70 μm and 100 μm, respectively. Both the electrodes and the electrolyte layer thickness has to be reduced in a further optimization process. The thickness of the electrolyte layer to be aimed at is about 30 μm, the thickness of the electrode layers about 50 μm.

CONCLUSION

The fabrication of the entire MEA multilayer arrangement by means of vacuum plasma spraying in one consecutive process has been presented. The application of the VPS technique demands a modified new cell design with a supporting porous substrate which also enables a very thin electrolyte thickness.

Further work with vacuum plasma spraying of MEA compounds has to be done with respect to the optimization of thickness and microstructure of the layers. The layers themselves and the transition between the different layers can be further improved by grading in composition and porosity in order to extend the three-phase boundaries and to improve long-term stability. For this reason, the evaluation of the electrochemical performance of plasma sprayed cells has to be carried out urgently. Based on these results the next stages towards the economical production of SOFC components in a consecutive spray process will be performed.

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Fig. 1: Principle of a MEA design for SOFC, adapted for production by vacuum plasma spraying

Fig. 2: SEM micrograph of a dense VPS-YSZ electrolyte layer
Fig. 3: Metallographic cross section of a graded VPS-Ni/YSZ anode layer

Fig. 4: SEM micrograph of a porous VPS-La$_{0.8}$Sr$_{0.2}$MnO$_3$ cathode layer

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Fig. 5: Metallographic cross section of VPS-Ni/YSZ anode - YSZ electrolyte layers on a nickel felt substrate

Fig. 6: Metallographic cross section of a VPS multilayer arrangement consisting of a Ni/YSZ anode, a YSZ electrolyte and a La₀.₈Sr₀.₂MnO₃ cathode layer on a nickel felt substrate