JTTEE5 17:598–602
DOI: 10.1007/s11666-008-9248-3
1059-9630/$19.00 © ASM International

Technical Note

Development of a Functional Sealing Layer for SOFC Applications

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(Submitted June 26, 2008; in revised form September 30, 2008)

Solid oxide fuel cells (SOFCs) are widely considered as an alternative solution to the decrease in fossil energy consumption. However, to achieve high efficiency and long-term stability for a SOFC stack, it is essential to maintain a stable hermetic seal. To obtain efficient air tightness between two SOFC cells, a solid seal composed of a ceramic matrix charged with glass particles has been developed. Atmospheric plasma spraying was selected to produce the solid seal because it can be used on a wide range of substrates of various natures and shapes. The developed seal was found to be solid, undistortable, and adhesive to its support at ambient temperature. The sealing properties were acquired when the SOFC was put into service: the glassy phase migrated into the peculiar plasma-sprayed microstructure of the ceramic matrix toward the interface leading to the air tightness of the deposit. The performance of the seal was: the leak rate observed at 7 kPa was 0.43 Pa L/s and, as a comparison, the requirement of the US Department of Energy is 0.5 Pa L/s.

Keywords ceramic matrix, glass compound, sealing, SOFC

1. Introduction

Solid oxide fuel cells (SOFCs) are promising energy conversion devices that produce electricity by an electrochemical reaction of a fuel gas, such as hydrogen or methane, with oxygen (Ref 1). Besides a highly efficient process, advantages of SOFCs include low emission rates of air pollutants, the ability to use high-temperature exhaust for cogeneration or hybrid applications, and the ability of internal reforming (Ref 2). This family of fuel cells is mainly dedicated to high-power applications and mobile auxiliary power units.

Whether in the form of a stack or individual cells, it is essential that the fuel and oxidant be kept separate from one another. Otherwise, the efficiency in producing ion exchanges across the electrolyte would be lowered and there would be a strong risk of exothermal explosions. Generally, the required sealant characteristics include the following (Ref 3): coefficient of thermal expansion well adapted to the other components to minimize thermal stresses and to improve thermal cycling behavior, sufficient fluidity to seal gaps at the sealing/assembly temperature, tailored viscosity at the operating temperature, gastight/marginal leak rate, thermal as well as chemical stability, electrical insulation, low cost, and flexibility with regard to design.

This generic set of requirements is not an exhaustive list because the characteristics of the sealant are also linked to the operating conditions of the stack.

Both rigid and compressive seals are being developed to meet the challenge of the hermetic device, essential for the development of planar SOFC (Ref 4). A recent review by Fergus on this subject explained the differences between various seals and presented both advantages and drawbacks (Ref 5). A major advantage of compressive seals is the fact that they are not rigidly fixed to the other SOFC components. Thus, an exact match of the thermal expansion is not required. However, a constant pressure must be applied to operate the gas-tight function during operation. For an effective compression, the seal must deform in response to the applied stress. So the main directions for the technical development consist in using ductile metals (Ref 6), materials of deformable shapes, or mica-based materials (Ref 7). On the other hand, rigid seals, which are mainly constituted of glass (Ref 8) and glass-ceramic sealants or metallic brazes, do not require this applied pressure. They have more stringent requirements for adherence, cracking and thermal expansion matching. However, the main advantage of glass seals is the possibility to adapt the glass composition to get optimized physical properties (Ref 9, 10). To go beyond the stress caused by differences in thermal expansion coefficients, fiber-reinforced glass seals have been studied. Their advantages are a certain elasticity at the operating

This article is an invited paper selected from presentations at the 2008 International Thermal Spray Conference and has been expanded from the original presentation. It is simultaneously published in *Thermal Spray Crossing Borders, Proceedings of the 2008 International Thermal Spray Conference,* Maastricht, The Netherlands, June 2-4, 2008, Basil R. Marple, Margaret M. Hyland, Yuk-Chiu Lau, Chang-Jiu Li, Rogerio S. Lima, and Ghislain Montavon, Ed., ASM International, Materials Park, OH, 2008.

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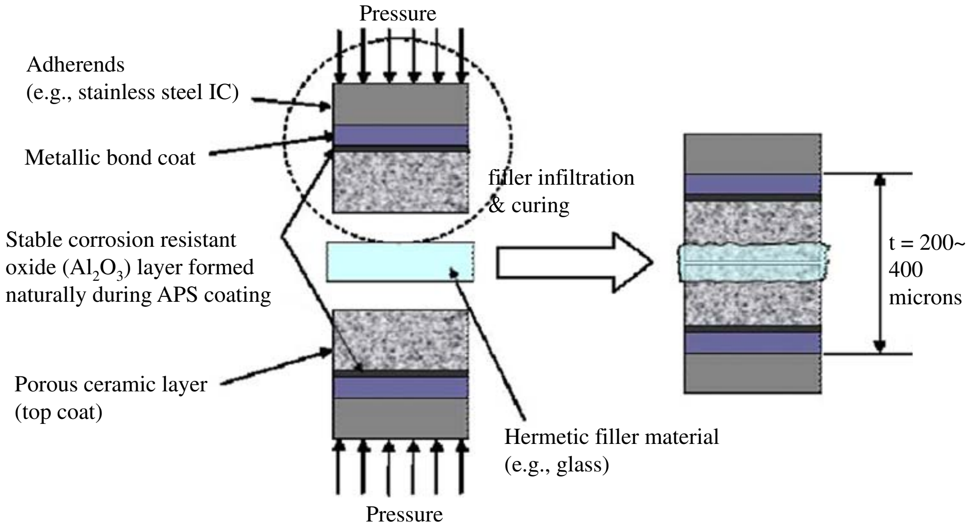

Fig. 1 Scheme of the conceptual structure of the integrated composite seal (Ref 13)

temperature and a better compatibility with the thermal cycles of the SOFCs (Ref 11, 12).

The main processes used for elaborating glass seals are screen printing or pneumatic spraying. In the case of fiber seals, a mechanical pre-compaction allows to elaborate auto-structured seals. In the literature, only a single report mentioning the use of plasma spraying could be found. Huang et al. (Ref 13) investigated a multilayered composite seal structure consisting of thin layers of oxidation-resistant metals, porous ceramics, and fillers/glass as shown in Fig. 1. The seal is an integrated part of the interconnected cells since it is directly coated onto the surfaces of matching parts owing to the use of atmospheric plasma spraying. During the stack assembly, the cells were joined through a heat/pressure-assisted curing process. The coating demonstrated an excellent mechanical robustness (thermal shock, tensile adhesion), high electrical resistivity, and low gas permeability.

The seal developed at the Laboratory of Thermal Spraying in CEA (Monts) differed rather significantly from those previously reported, and has led to a patent filing (Ref 14). The plasma spray technique (Ref 15) was used to elaborate a coating composed of glassy particles dispersed into a matrix that remained solid during high-temperature operations.

Details of elaboration as well as the mechanisms are presented in the next sections. Moreover, initial tests with regard to the leak rate and thermo-cycling resistance are reported.

2. Experimental Procedure

The materials were selected according to their coefficients of thermal expansion (CTE), which is one of the fundamental characteristics for an efficient seal. The ceramic matrix was ZrO_2-8wt.%Y_2O_3 (particle size range 5-25 μm, Medicoat France). Whereas the glassy compound was a borosilicate (particle size range 2-22 μm, DMC[2] France S.A). Its detailed composition (supplier data) was B_2O_3 36 wt.%, SiO_2 31 wt.%, Na_2O 16.7 wt.%, CaO 7.6 wt.%, MgO 3.6 wt.%, and Al_2O_3 0.87 wt.%.

The properties of this glass are: half-sphere temperature = 710 °C; softening point under pressure = 580 °C; and thermal expansion coefficient = 8.9×10^{-6} K^{-1}. The half-sphere temperature is the temperature at which the sample changes its shape so that its base radius equals its height, taking the shape of a half-sphere.

Boron oxide is an important additive to silicate glasses since it decreases the glass viscosity, as well as the softening point and glass transition temperature of the SOFC sealant (Ref 16). The presence of calcium and magnesium in the C105 is known to promote adherent and stable interfaces with yttria-stabilized zirconia (YSZ) (Ref 17).

The composite powder was manufactured by mechanically blending 20 wt.% glassy C105 compound with ceramic YSZ powder. The choice of the plasma spraying process was dictated by the need for cost reduction compared to other manufacturing routes. Atmospheric plasma spraying (APS) was carried out with an automatic plasma system equipped with a Sulzer-Metco F4VB plasma gun (Wolhen, Switzerland), a turntable, and a six-axis robot. The plasma spray parameters were optimized with respect to the Ar/H_2 working gases, the spray distance, and the powder injection.

The APS seal was characterized with scanning electron microscopy (SEM) in back-scattered electron (BSE) mode to differentiate the different components while the porosity and the glass percentage were measured by the combination of two techniques: Archimedes Porosimetry and Helium Picnometry. These volumetric methods involved the elaboration of free-standing samples.

3. Principles of the Plasma-Sprayed Seal

As shown in Fig. 2, the coating consisted of flattened droplets with interlamellar contacts, microcracks, and globular porosities. The total void content of this typical APS coating is around 13%. The percentage of glass compound after plasma spraying is more important (up to 40%) than the one contained in the blending feedstock because of a heterogeneous treatment in the plasma jet. Unfortunately, the weak contrast difference does not allow highlighting this phenomenon. However, some glass inclusions could be seen forming dispersed within the matrix of YSZ droplets.

In fact, during the SOFC operation, the glass compound softened whereas the matrix remained solid. Owing to a low viscosity and no reaction with the YSZ matrix, glass could migrate by capillarity through the three-dimensional network of interconnected cavities toward the free surface of the ceramic matrix involved in the glassy seal coating. At the same time, the glass filled most of the defects linked to the plasma spraying process. This gave rise to a continuous network and effectively blocked the continuous 3D leak path.

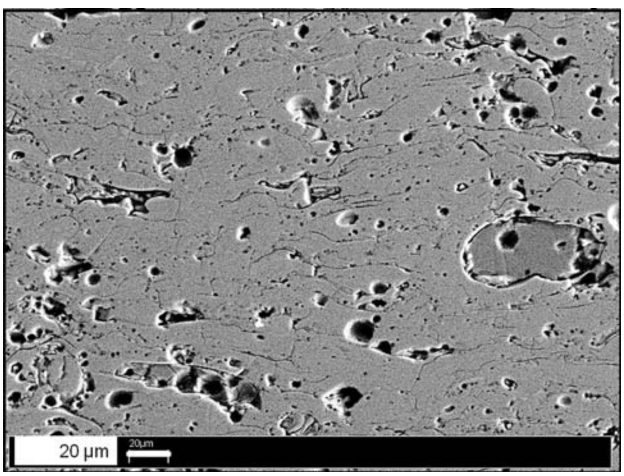

Fig. 2 SEM image of a cross section of the plasma-sprayed seal

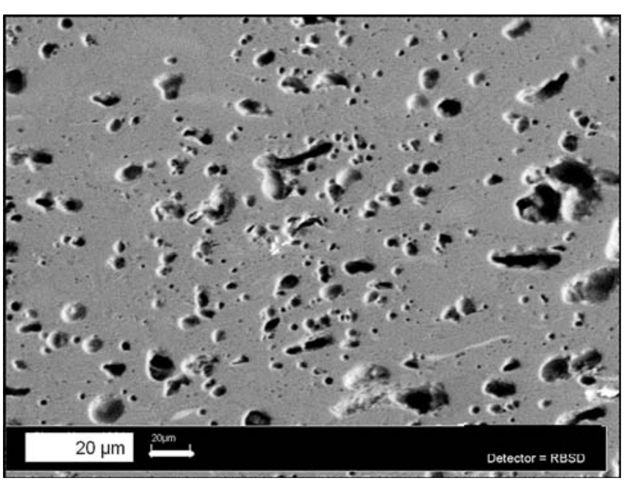

Fig. 3 Cross section of a plasma-sprayed seal after annealing at 900 °C during 30 min in air

Figure 3 displays a SEM image of a cross section of plasma-sprayed seal after annealing during 1/2 h at 900 °C in air. Due to the poor optical contrast between the glass compound and the ceramic matrix, the plasma-sprayed microcracks that are usually filled with glass were no longer visible. The only thing that remained was a closed porosity linked to cavities that initially contained the glass compound, but were emptied due to the glass migration. The overall porosity remained constant.

4. Characterization of the Plasma-Sprayed Seal

4.1 Leak Rate Measurements

To qualify leak rate of the plasma-sprayed seal, the "pressure loss" method was chosen. This method allows the measurements at the SOFC operating temperature. The setup for the leak rate test was composed of a gas feeder, an insulation valve, a data recording system, a buffer volume, and an oven that was able to reach a temperature of 1200 °C. The seal (thickness = 150 µm) was produced on a conical form corresponding to the tested design, on which a load of 19.6 kPa was applied (Fig. 4).

The seal was heated to 900 °C at 2.5 °C/min. After the furnace reached the desired temperature, the inner part of the conical form was flushed with nitrogen to perform the sealing tests for several pressure differentials as shown in Fig. 5.

Three domains were observed: [0-40 kPa]: leak rate ranged between 0 and 2.4 Pa L/s; [40-70 kPa]: leak rate was stabilized; [>50 kPa]: leak rate showed a linear increase from 3.15 to 5.94 Pa L/s.

According to the US Department of Energy, the requirement of a good sealing is 0.5 Pa L/s under a differential pressure of 7 kPa. The plasma-sprayed seals obtained in our work resulted in the leak rate of 0.43 Pa L/s and are therefore suitable for application in SOFC.

4.2 Thermal Cycling

Thermal cycle testing was conducted by heating the specimen in air at a rate of 2.5 °C/min to 900 °C, keeping constant this temperature for 30 min, and then cooling to ambient temperature, under a pressure differential of 20 kPa, before reheating under the same conditions. No degradation of the leak rate was observed after four cycles.

4.3 Rupture Strength Test

The second application of this particular plasma-sprayed seal in the possibility is to join two interconnectors in a SOFC stack as shown in Fig. 6. The seal was plasma sprayed onto the first sand-blasted and degreased

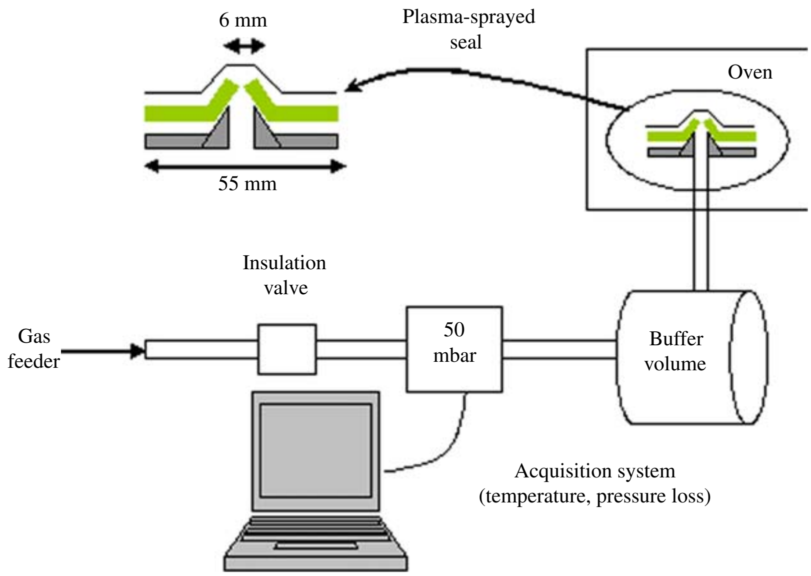

Fig. 4 Experimental setup for leak rate testing

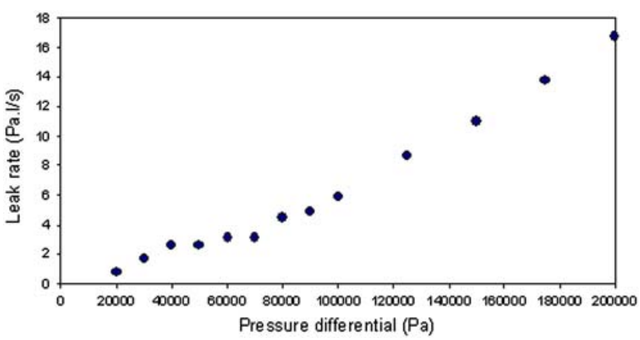

Fig. 5 Measured leak rate as a function of pressure difference

interconnector (CROFER APU 22-Thyssen Krupp), and the second interconnector was placed on the free surface of the plasma-sprayed seal. At the conditioning temperature (900 °C) after a heating rate of 2.5 °C/min, due to its viscous flow, the glass compound filled the free space between the two pieces giving rise to an air-tight layer as shown in the top part in Fig. 6.

To quantify the rupture strength of the joining, a test was developed. It consisted of clamping the bonded assembly into a fixture then increasing the air pressure until the interface, composed of the seal between the two interconnectors, breaks. The rupture pressure for a seal with a thickness of 220 μm was measured to be around 250 kPa.

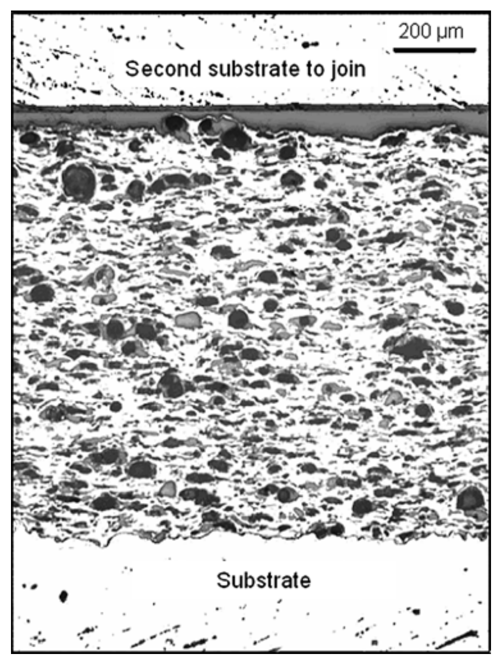

Fig. 6 Optical micrography of a cross section of two surfaces (CROFER 22 APU) joined by the migration of the glass compound from the plasma-sprayed seal

5. Conclusions

One of the challenges for implementation of SOFCs relies in maintaining a hermetic sealing that remains resistant and stable over the lifetime of the stack. To efficiently and hermetically join two SOFC repetitive units or components, a plasma-sprayed solid seal constituted of a ceramic matrix charged with glass particles was developed.

This seal was found to be solid, undistortable, and bonded to its support at ambient temperature. It could also be realized as a self-supported body with a thickness from 50 μm to several millimeters.

Even though the initial structure of the plasma-sprayed seal was microcracked, the principle of the glass filler migration leads to an increase in the gas tightness of the matrix and to the possibility of sealing two surfaces owing to the glassy coating at the free interface.

This seal was tested in a stack of five SOFC cells under normal operating conditions. The performance of the stack was nominal and no internal combustion between hydrogen and oxygen was observed.

Acknowledgments

The authors wish to thank Mr. Bories and Mr. Toulc'hoat for their contribution in the development of the seals and Dr G. Renouard-Vallet for her help in the testing of the plasma-sprayed seals.

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