Procedures for glass sealant material investigations

Introduction:

This document reports the detailed procedures for the characterization of glass sealant materials. Such investigations have the aim to help in the selection of suitable compositions for application in SOFC stacks. For this purpose it is necessary to study the evolution of both the bulk characteristics (i.e. crystallinity, porosity, precipitates, cracks) and the interface ones (i.e. layer formation, element diffusion, delamination). The reproducibility and representativeness of the samples have to be granted adopting suitable sample designs. The tests reliability has to be easily compared with results coming from post-experiment stack characterizations.

The sample preparation, starting from raw materials will be following described, together with a detailed description of the samples design, the testing parameters and the criteria for the glass sealing composition choice in the frame of the project ENDURANCE.

1. Samples preparation

1.1 Paste preparation

Glass compositions, supplied in form of powders, have to be mixed with an organic binder terpineol- based to obtain a slurry.

The proportion powder/binder is a critical factor for the sample preparation and its final properties. The quantity of binder could influence the porosity in glass-bulk and the adhesion between glass and steel. Gasses released by binder during the curing treatment could be removed through a porous network depending on the granulometry of the glass powders, applied mechanical load and amount of binder present in the mixture. Additionally, a suitable powder/binder ratio ensures proper application of the mixture on the substrate and handling of the sample. Such proportion depends on the granulometry of the glass powders: higher amount of binder is required for lower particle sizes since the increase of the powder surface area.

For reference, preparing the mixtures using glass powders particle sizes d_{50} ~ 40μm and d_{99} ~ 150 μm the powder/binder ratio is approximately 10/1. It has to be adjusted for every composition in order to obtain a dense paste. Such consistency prevents the paste to flow from the substrate changing the sample geometry and ensures the proper application and handling.

Before the application, the mixture has to be homogenized using a mechanical blender and ultrasonic bath to remove gas bubbles.

1.2 Substrates preparation

The sample assembly includes metal substrates on which the glass paste is applied. For each sample design the substrate thickness and surface finishing are constant. In this series of analysis, such features consisted of a thickness of 0.5 mm of the metal sheet and no surface changes after the cold rolling applied by the steel producer. To avoid contaminations at the interfaces, the substrates are ultrasonically cleaned (600W, 40kHz) for 5 minutes in acetone and 5 minutes in deionized water.

1.3 Samples design

Four different sample designs (Figure 1) have been optimized based on the type of test and the equipment:

a) Steel/glass/steel

This geometry, consisting of two square metal plates (10mm x 10mm) bonded using a glass sealing layer is used to check the evolution of the glass/metal interfaces in single atmosphere (i.e. static air) with and without the application of an electrical load. Such test allows to investigate changes in the interfacial adhesion, element diffusion between the involved materials, the formation of additional layers and the evolution of the electric resistance of the glass.

b) Steel/YSZ/glass

This sample consists of a glass sealing layer applied on a square metal plate (10mm x 10mm) previously coated with a YSZ layer. Such configuration is used to check the compatibility between the glass and YSZ, the evolution of the steel/YSZ and YSZ/glass interfaces and the YSZ effectiveness as barrier layer preventing the diffusion of metal ions within the glass.

c) Steel/glass

This geometry is a simplified version of the first one (a). It consists of a glass layer on a square metal plate (10mm X 10mm). Exposing such sample to a single atmosphere is possible to test the compatibility of the glass with the substrate and observe the evolution of the elements diffusion at the interface and the bulk glass crystallinity.

d) Steel (circular crown)/glass/steel (disc)

This sample is optimized for tests in double atmospheres. It shows two interfaces to atmosphere in comparison to the first one (a). The sealing is used to bond a circular crown to a disc which are exposed to different gas streams: the top side of the disc and the crown, together with the external part of the glass are exposed to an air flow. The bottom side of the disc and the crown, together with the internal side of the glass are exposed to a fuel stream (i.e. H_2/N_2 humidified mixture). In this way is it possible to evaluate the dual atmosphere effects at the interfaces and through the sealing section. Additionally, such geometry allows to measure the glass layer electrical properties.

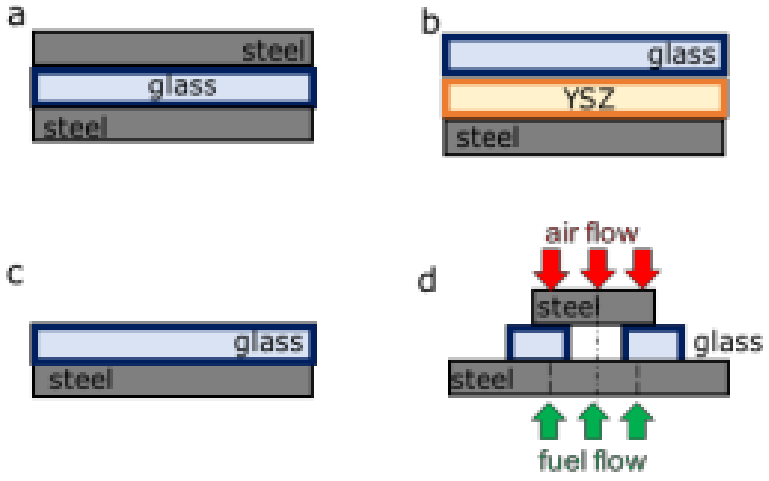

Figure 1 – Cross section draws of samples employed for tests in single (a-c) and double (d) atmospheres.

1.4 Assembling and curing of samples

When required, a flux has to be applied on the metal substrate before the sample assembling. When the substrates are prepared, a homogeneous glass paste layer is applied using a spatula on them.

The application of a weight on the assembled sample can be required to improve the glass adhesion on the substrates and the removal processes of burnout of the organic binder. Weights have to be constituted of refractory materials to withstand to the thermal treatments temperatures. To reduce the inhomogeneity of the glass layer thickness, refractory materials spacers can be placed between the two substrates keeping them parallel and at the same distance.

After the samples preparation, glasses have to be cured following the thermal treatment suggested by the supplier. Such treatment, performed in static air, usually requires more steps of heating and dwell at certain temperatures with controlled ramp speeds.

2. Tests

The curing treatment itself is already the first part of test giving information about the compatibility of the glass with the substrate in terms of adhesion. Additionally, the characteristics of the sample (glass/steel adhesion, glass microstructure and steel oxidation) after the curing treatment can be considered as the initial state of the sample, to be compared with samples exposed to different SOFC working conditions and testing times. This comparison allow to observe the influence of time and working parameters to the evolution of the sample features.

Types of tests are summarized below:

➢ Curing treatment: It lead to the removal of the binder and sintering of the glass powders. The sample cured is named "**Green**" in this document and it represents the zero-state of the glass.

➢ Oxidation in static air: It consists in the aging of the sample at a selected SOFC operating temperature (780°C in the frame of the project ENDURANCE). "**Oxidized samples**" are characterized after several exposure times: 100, 250, 500, 750, and 1000 hours, in single atmosphere (air).

➢ Oxidation under an electrical load: Consists in the aging of samples following the guidelines of the oxidation in static air with the addition of a polarization of 0.8V for exposure times of 100 and 250 hours. **Polarized** samples have to be connected through two Pt wires to a potentiostat. Two additional Pt wires (connected to a multimeter following the 4-wires circuit) are required to measure the sample resistance.

➢ Oxidation in dual atmosphere: This is the aging of the sample exposed to a dual atmosphere (Air/H_2 humidified with 48%H_2O).

3. Equipments

3.1 Green and Oxidized samples

A furnace, capable to heat up to 900°C with controlled heating and cooling rate is needed for the curing treatment of the samples and to perform the oxidation tests in single atmosphere. Temperature variations of 2 or 5°C min^{-1} are required during the curing treatment

depending on the protocol provided by the powder supplier. Samples are then heated/cooled using temperature variations of 2°C min^{-1} to avoid thermal

3.2 Polarized and Dual atmosphere samples

Polarized and dual atmosphere samples need to be electrically contacted to a potentiostat and a multimeter, therefore the testing furnace have to be equipped with ducts that allow the introduction of up to 4 insulated Pt wires. Such wires are spot-welded to Pt nets which provide the electric contact to the sample.

Additional characteristics are required for the tests in dual atmosphere, where the gases have to be kept separated to avoid combustion reactions between the fuel and the oxygen contained in the air stream (Figure 2).

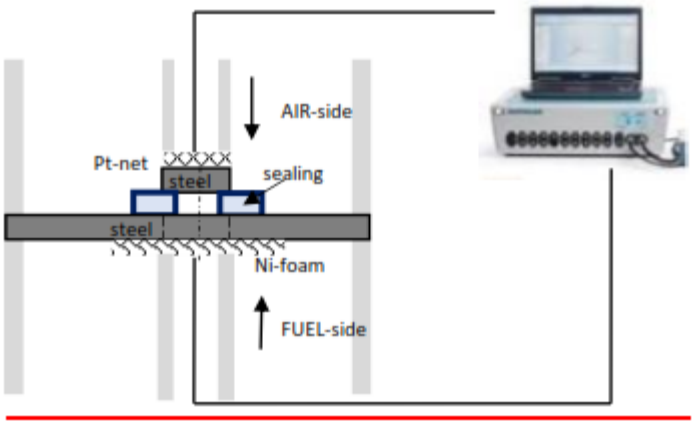

Figure 2 – Drawing of the test setup for dual atmosphere tests

4. Post-experiment characterization

For the post-experiment investigations, samples have to be epoxy mounted using a resin which polymerizes at room temperature and atmospheric pressure. The use of increased temperature and pressure could lead to cracking of the glass layer. Samples are then cut to expose their cross section and polished using SiC paper from 180 to 1000 grit and then finished with a diamond suspension of 6, 3, 1 and 0.25 µm.

For the interfacial characterization, a scanning electron microscope, equipped with the energy dispersive spectroscopy (EDS) detector, is used. Before the microscopic observation, samples have to be coated with 5 nm of gold (or carbon) by magnetron sputtering to enhance their electron conductivity. EDS linescans at the interfaces highlights the diffusion of elements from the substrate toward the bulk of the glass layer.

SEM-BSE pictures at 5000x have been used to estimate the crystallinity and the porosity of glass using the Software ImageJ. Such characteristics have been measured on four square portions 60x60 µm of the glass bulk for each sample using the *Threshold* tool and selecting the grey scale interval corresponding to the phase under investigation.

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