Development of sealing layers for the integration of Oxygen Transport Membranes in a planar separation module

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Abstract

Oxygen Transport Membranes (OTMs) are dense ceramic structures that can conduct both electrons and oxygen anions, provided that they are exposed at high temperature (T > 700 °C) and an oxygen partial pressure gradient. Owing to this property, OTMs can separate oxygen from air with theoretically infinite selectivity. Separation based on OTMs can be used to provide pure oxygen in oxy-fired industrial processes, leading to possible energetic and economic savings with respect to energy-intensive conventional cryogenic techniques like Air Separation Unit (ASU), Pressure Swing Adsorption (PSA) and Vacuum Swing Adsorption (VSA) [1].

In order to integrate OTM technology in industry, it is necessary to develop monolithic modules where the ceramic membranes are housed and sealed to a metallic frame. This entails several technological challenges, including the identification of junction layers able to connect two materials with different nature (i.e. a metal and a ceramic material) providing gas tightness, adequate mechanical strength and both thermo-mechanical and chemical stability at the high operating temperature. Such requirements can be mitigated when using tubular membranes, since the temperature of the sealings can be lowered by means of cooled flanges. However, this also causes the cooling of the membrane regions adjacent to the junctions, resulting in an undesired reduction of the effective membrane area available for the permeation and, in turn, of the total oxygen flux. Differently, in planar modules the entire volume of the membranes is maintained at the operating temperature and the whole membrane area contributes to the permeation, but the metal-ceramic junctions must withstand more severe conditions.

In this work, we focused on the development of sealants for metal-ceramic interfaces, needed for the fabrication of a prototypal OTM module with planar geometry [2]. The device consists of an Inconel 625 metallic housing and a membrane component made of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) (Fig 1), which was selected as OTM material since it combines high permeation fluxes and satisfying chemical stability during operation.

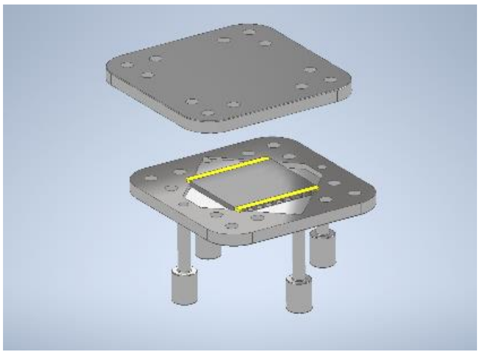

Fig. 1 Drawing of the prototypal OTM module, consisting of a metallic frame – here shown opened – and a LSCF membrane component. The metal-ceramic joining regions are highlighted in yellow.

For the realization of the junctions we used glass-ceramic composites, which are promising for such application thanks to the possibility to adjust their thermal expansion properties by tailoring the composition. In particular, we investigated a custom-made Ba-based borosilicate glass (GC2), obtained in form of powders. For comparison, additional tests were made using a commercial glass tape.

Preliminary characterizations allowed us to identify the best sinter-crystallization treatment for GC2. In as-joined samples, the glass-ceramic layer showed good adhesion and chemical compatibility both with metal and ceramics. However, after an ageing for 7 days at 800 °C, the junctions were broken, possibly due to the growth of NiO at the

Inconel 625/GC2 interface. Feasible strategies to avoid this issue include (i) the replacement of Inconel by a different metal suitable for high T operations, e.g. Crofer22APU stainless steel, and (ii) pre-oxidation treatments of Inconel to form a protective Cr_2O_3 scale on the surface.

Besides, we observed that the precise control of thickness and uniformity of the sealant are crucial to obtain junctions without ruptures. Therefore, we tested an additive manufacturing approach to improve the accuracy of the glass deposition. We developed a GC2 paste with appropriate rheological behavior for a robocasting process and optimized both printing and post-printing steps. We realized 3D printed LSCF/GC2/Crofer22APU junctions with a configuration reproducing that of the final module (Fig. 1) and observed that, after sinter-crystallization, sealant stripes retain the desired geometry and do not show any macroscopical cracks, as revealed by computed X-ray tomography characterization done at J-Tech@PoliTO (Fig. 2).

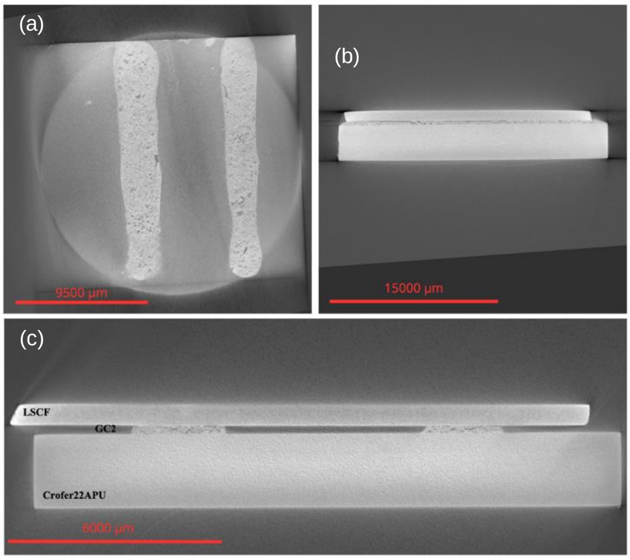

Fig. 2 Computed X-ray tomography pictures of LSCF/GC2/Crofer22APU junctions realized by depositing the sealant by robocasting: (a) top, (b) side and (c) front view.

Such results highlighted that scalable and cost-effective 3D printing technologies can be successfully applied for the manufacturing of patterned metal-ceramic joints with accurate spatial distribution.

Currently, tests of prolonged exposure at high temperature are ongoing on both LSCF/GC2/Crofer22APU and LSCF/GC2/pre-oxidized Inconel 625 junctions, to assess the resistance of the sealings and identify possible degradation mechanisms. The mechanical strength of as-joined and aged samples is also under investigation.

References

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[2] Drago, F., Fedeli, P., Cavaliere, A., Cammi, A., Passoni, S., Mereu, R., De La Pierre, S., Smeacetto, F. and M. Ferraris, "Development of a Membrane Module Prototype for Oxygen Separation in Industrial Applications", Membranes, 167-195, 12 (2022)