Development of hydrogen separation membranes by the PS-TF process

Introduction

The main objective of DEMOYS is the development of thin mixed conducting membranes for O_2 and H_2 separation. These membranes are obtained by deposition of a dense layer of the mixed conducting material on a porous support, by using the *"Low Pressure Plasma Spray – Thin Film"* (PS-TF) process.

The results of the activity regarding H_2 membranes development are summarized in this document.

Results

$La_{5.5}WO_{11.25-\delta}$ (LWO) was selected as reference material for H_2 separation membranes. This material presents an important ambipolar conductivity and is stable under CO_2 containing atmospheres.

Several batches of LWO powders have been manufactured by Sulzer in a prototype plant (up to 27 kg for a single batch). The main steps of the manufacturing process are shown in Fig. 1.

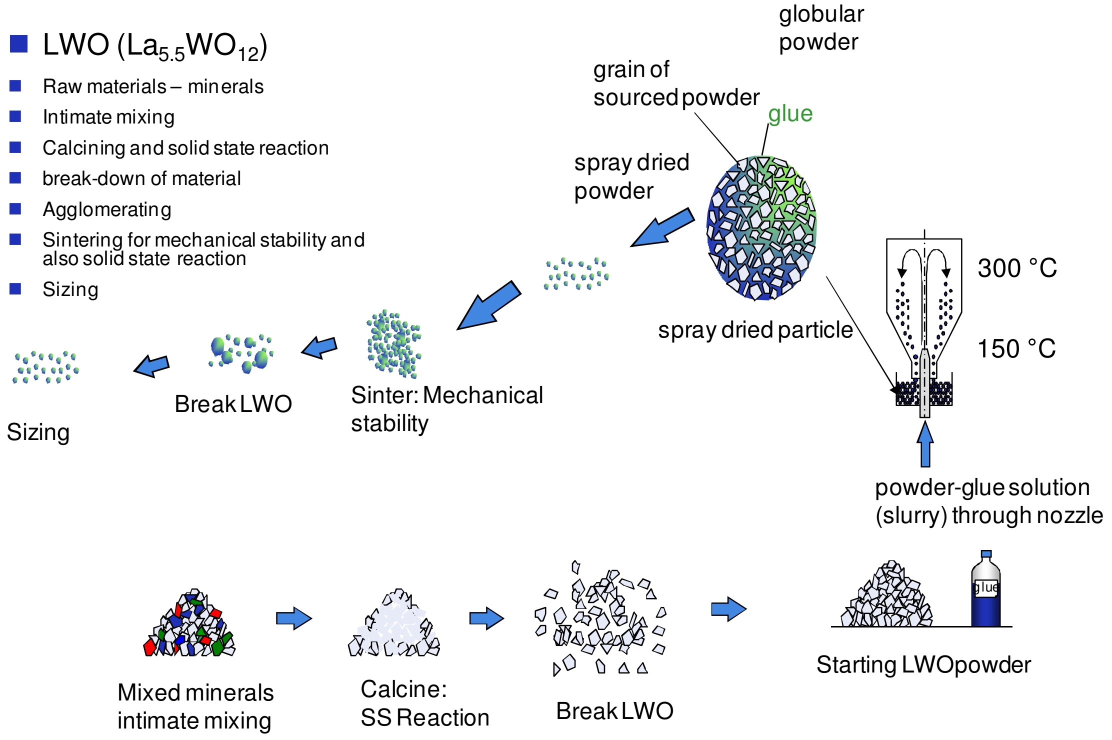


Fig. 1 Main steps of the manufacturing process of powders suitable for PS-TF process.

Induced coupled plasma (ICP) and X-ray fluorescence spectroscopy (XFS) have been used to determine the elemental composition of the powders, while structural and morphological characterization has been carried out by XRD and SEM analysis. Results indicate that synthesized powders meet specification requirements for the PS-TF process in terms of average particle size and particle size distribution, and show sufficient phase purity.
Moreover total conductivity of the powders synthetized by Sulzer, measured in H_2+H_2O and D_2+D_2O, is of the same order of magnitude as the reference lab sample.
Hydrogen permeation tests were initially performed with 1mm-thick pressed pellets made of LWO manufactured by Sulzer. Measured hydrogen flows are in the same range as reference lab sample (see Fig. 2). Based on these results, a H_2 flow of the order of 1mL·min^{-1}·cm^{-2} at 900°C is expected for a thin LWO membrane.

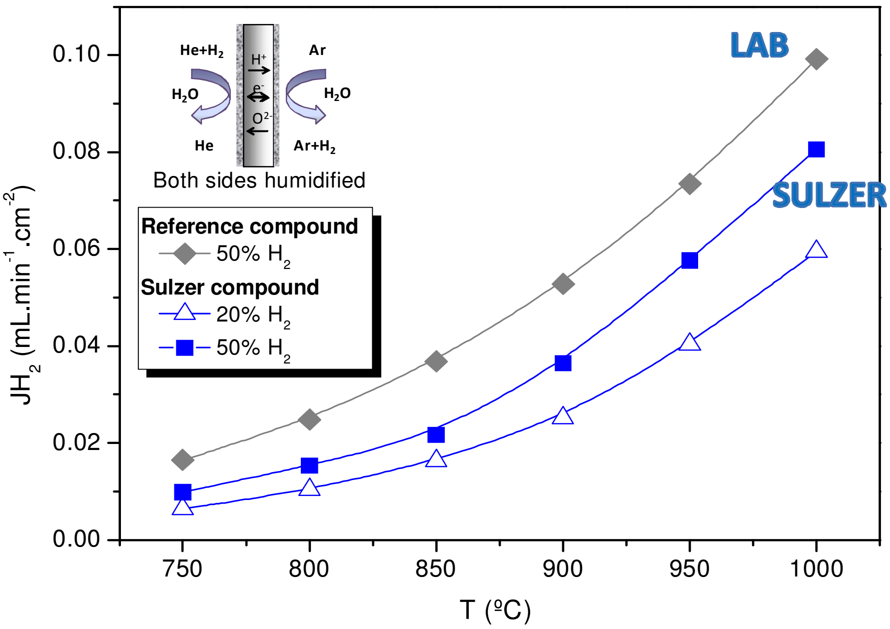


Fig. 2 H_2 permeation flow of LWO bulk samples (1mm thick) obtained with Sulzer and reference lab powders.

As a next step, LWO asymmetric membranes, 50 µm thick, have been obtained by Low Pressure Plasma Spray (PS-TF process) on planar NiCoCrAlY supports developed inside the project. Porous disks up to 110 mm in diameter have been sprayed. Process parameters have been optimized in order to obtain target composition and crack-free structure.

However very low hydrogen flow was achieved in membrane permeation tests (see Fig. 3), almost two order of magnitude lower than the expected.

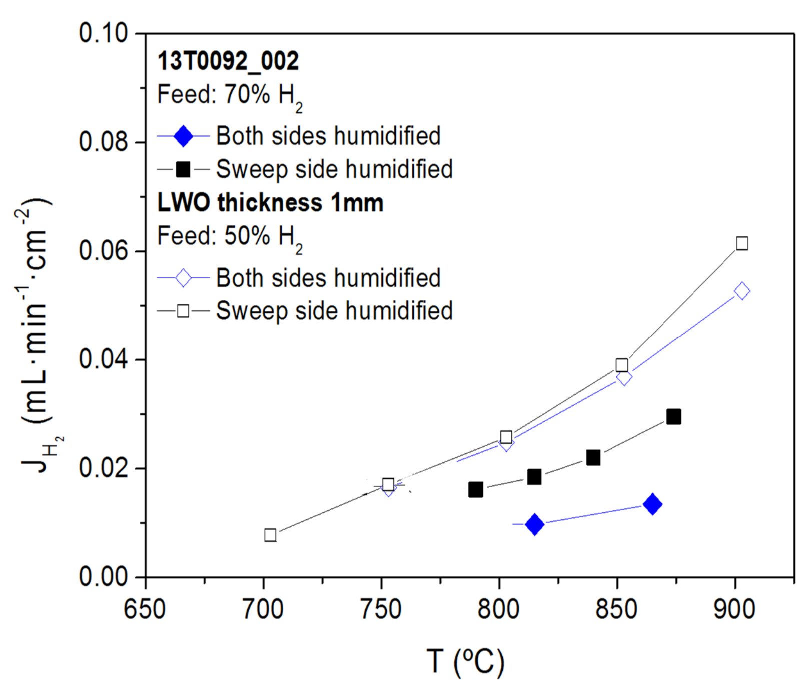
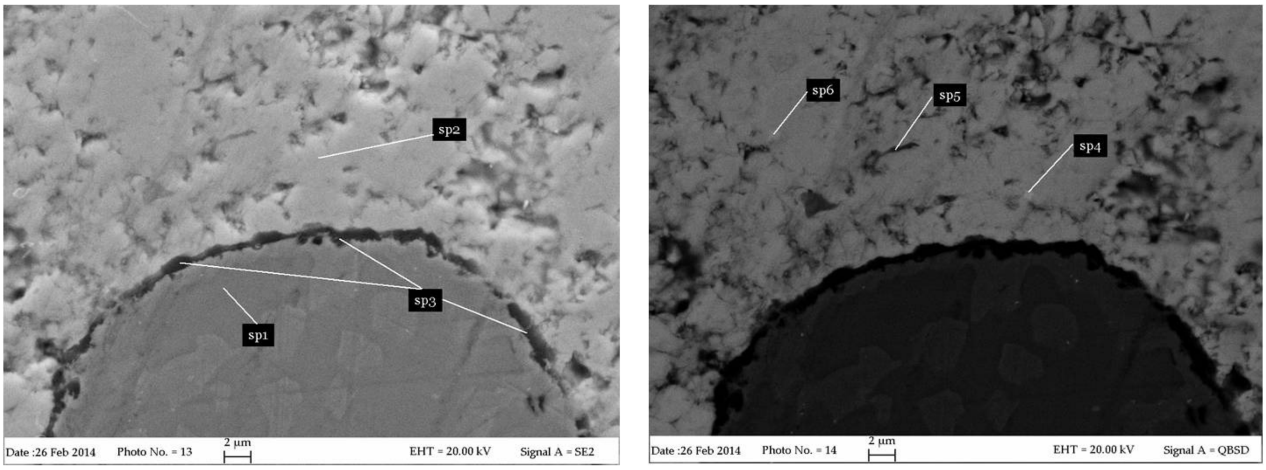


Fig. 3 H_2 permeation flux of a 50 μm asymmetric LWO membrane and a 1mm bulk samples

Metallographic investigations (SEM and XRD) evidenced the presence of phase segregations inside the LWO coating layer. In respect to the expected ratio La/W 5.5, values such as 2.5 or 14 have been detected (see Fig. 4). The phases with lower or higher La/W ratio are much less conductive than $La_{5.5}WO_{11.25-\delta}$ and this could explain the low membrane permeation. Several attempts have been made to overcome such a problem by varying spray parameters during membrane preparation; a different support material has also been used. Despite these attempts, no significant improvement in membrane permeation has been obtained. It has been concluded, therefore, that PS-TF process is not suitable for manufacturing LWO asymmetric membranes on metallic supports.

Consequently research effort of DEMOYS have been focused on O_2 separation membranes where very promising results in terms of permeation flux have been obtained.



Spectrum	1	2	3	4	5	6
La/W	/	4.6	12.1	2.9	4.7	3.5

Figure 4 SEM /EDS analysis of a LWO membrane

Conclusions

Asymmetric H_2 separation membranes have been obtained by deposition of a thin dense LWO layer on a porous metallic support by using the PS-TF process.

LWO powders used for the spray process have been manufactured by Sulzer in a prototype plant. These powders meet specification requirements for the PS-TF process in terms of average particle size and particle size distribution, and show sufficient phase purity and good ambipolar conductivity.

However low hydrogen permeation flow have been obtained with LWO asymmetric membranes; in-depth micro-structural analysis suggest that the PS-TF process is not suitable for manufacturing such a type of membranes.

Doping of LWO and/or the use of different mixed conducting materials could be pursued in the future as a research topic, to further assess the possibility of obtain high performance hydrogen separation membranes with the PS-TF process.