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POROUS NI SUPPORTS FOR THIN FILM MEMBRANES

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Abstract: Metal-supported solid oxide fuel cells (SOFCs) are promising due to their good mechanical and thermal properties. Stainless steels are often used as a supporting metal. In this study, the possible use of Ni as a supporting metal was tested. Spherical (purity 99.8 % of nickel), 5 to 15 μm particles and irregular (purity 99.99 % of nickel), particle size under 6 μm , of Ni powders were used. Porous nickel supports were successfully made by uniaxial pressing of nickel powders at 400 MPa of pressure, sintering was done in vacuum, 10^{-5} Torr at 550 °C. The sintering time was 60 minutes in order to obtain a high open porosity. Sintered samples were characterized by electron microscopy and mercury porosimetry.

Key words: Ni powder, porous supports, hydrogen separation membranes

1. INTRODUCTION

Variety of porous supports has been used for different alloy dense membranes recently. A lot of studies describe different methods to fabricate such composite membranes. The most common methods used to obtain these membranes are sputtering, electro less plating, CVD and electroplating [1-4]. The materials used for porous supports are ceramics, glass and stainless steel [2-9]. Recently, silicon wafer covered with SiO_2 and TiO_2 have been reported [10].

For high quality of metallic composite membrane the support should be porous, smooth facial, highly permeable, thermally stable and metallic adhesive. Furthermore, it has to have defect-free surface. Moreover, in order to produce the membranes in large quantity the method of fabrication should be as simple as possible. On the other hand, the thickness of the deposited film depends of the deposition method and the pore size of the support [1].

Uemiya [11] reported that the thickness of the deposited layer strongly depended on the supports quality, such as narrow pore size distribution and the amount of defects on the surface.

Among the supports, non-metal, such as ceramic and glass has weak adhesion to metallic thin film and difficulty to seal into commercial component. The weak adhesion, different thermal expansion coefficients and the volume change of the membrane in contact with hydrogen may cause stability problems [6, 9, and 12].

On the other hand, porous stainless steel support has been used to improve mechanical strength of the support. From the viewpoint of a practical application, porous stainless steel has the merit of getting more readily sealed into a commercial unit [1].

There are some applications of other metal supports. Zhang et al. [13] obtained Pd-Ag alloyed film on V-15Ni alloy. However, metallic interdiffusion and selective oxidation of vanadium deteriorated the Pd-Ag membrane. They insisted that the stainless steel with low hydrogen affinity cracks the palladium-based alloy film or become porous during hydrogenation/dehydrogenation.

Tosti [14] found that metals, such as Nb with hydrogen permeability higher than Pd crack the Pd-based alloy during hydrogen permeation. He suggested that nickel with lower permeability than Pd is a good metal for ideal permeation behaviour. However, since

they used dense nickel for support, hydrogen permeability was too low.

This paper focuses on the obtaining and characterization of porous nickel supports obtained by uniaxial pressing of spherical and irregular Ni powders in a cylindrical die having 11.3 mm in diameter.

2. MATERIALS AND EXPERIMENTAL METHODS

Spherical nickel powders (size range 5-15 μm) with a purity of 99.8 % of nickel and irregular nickel powders (under 6 μm) with a purity of 99.99 % of nickel were used as raw materials for porous nickel supports. The starting powders were studied by scanning electron microscopy (Fig.1). For each experiment 0.5 g of powders were used. The samples were obtained by compressing the Ni powders at 400 MPa of pressure. The obtained disks were than sintered in vacuum (10⁻⁵ Torr) at 550 °C for 60 minutes.

The sintered supports were analyzed by SEM. An image analysis software (ImageJ) was used to measure the surface porosity and pore size.

Pore size distribution, average pore size, total pore volume and porosity of the supports were measured by mercury porosimeter.

The pore tortuosity was calculated using the ecuation:

$$\alpha_p = \frac{S_p \cdot r_0 \cdot \rho}{2P} \quad (1)$$

where S_p is the specific surface, r₀ is the average pore radius, ρ is the bulk density and P is the total porosity [15].

3. RESULTS AND DISCUSSIONS

Spherical (5 to 15 μm), and irregular (under 6 μm) Ni powders (fig.1.) were used as raw materials for porous nickel supports.

The porous supports were made by compressing at 400 MPa of pressure the Ni powders in a closed die. The samples, 11.3 mm in diameter and ~ 1.4 mm thick (Fig.2.), were sintered in vacuum (10⁻⁵ Torr) for 60 minutes for mechanical strenght.

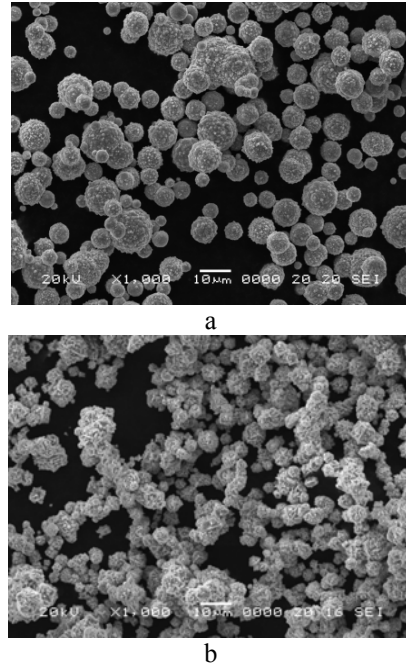


Fig.1. SEM images of the used Ni powders
a. spherical, b. irregular



Fig.2. Photograph of the developed porous Ni support

The sintered supports were studied by scanning electron microscopy (SEM), and as it is shown in Fig.3. the porous nickel supports have relatively small pores with uniformity and the surface is smooth enough that thin films can be deposited on it without surface modifications, but in the same time presents a porosity high enough to be permeable.

Comparing to commercial α-alumina and porous stainless steel, the surface of the porous nickel support is smooth enough and the pore diameter is so small as to apply the support for metallic dense membrane.

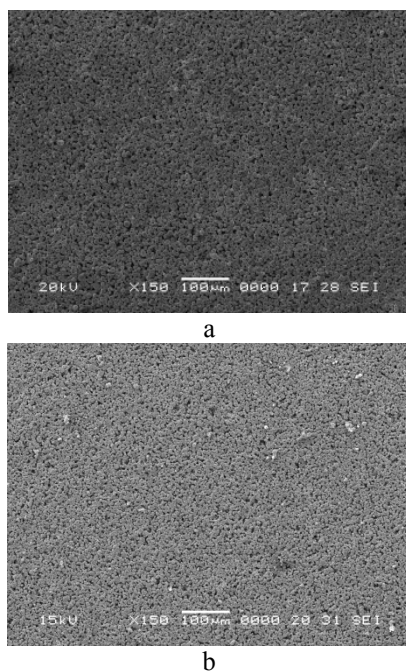


Fig.3. The SEM images of the developed porous nickel supports. a. spherical powder, b. irregular powder

After sintering the density and the porosity of the supports was calculated, the results are presented in Table 1.

Table 1

Calculated density and porosity of the Ni supports.

Powder shape	Compacting pressure [MPa]	Density [g/cm ³]	Porosity [%]
Spherical	400	6.17	31
Irregular	400	6.20	32

An image analysis software (ImageJ) was used to measure the surface porosity and pore size. This analysis was done on the SEM image presented in Fig.3. Tabel 2 presents the results of this analysis.

Table 2

Surface porosity and pore size of the Ni supports

Powder shape	Average pore diameter [µm]	Surface porosity [%]
Spherical	4.1	30
Irregular	4.6	22

* Compacting pressure 400 MPa

The porous nickel supports (compacted at 400 MPa) were than studied by mercury porosimetry, the porous nickel support made

from spherical powders has a total porosity of 29.45 % and an average pore diameter of 4.08 µm, while the support made from irregular powders has a total porosity of 34,47 % and an average pore diameter of 4,61 µm. The calculated tortuosity was 3,5 for the samples made of irregular powders and 1,7 for the samples made of spherical powders.

4. CONCLUSIONS

Spherical (size range 5-15 µm) with purity of 99.8 % of nickel and irregular (under 6 µm) with a purity of 99.99 % of nickel powders were used as raw materials for porous nickel supports. The samples were obtained by compressing the Ni powders at 400 MPa of pressure. The obtained disks were than sintered in vacuum (10^{-5} Torr) at 550 °C for 60 minutes.

The porous nickel supports have relatively small pores with uniformity and the surface is smooth enough that thin films can be deposited on it without surface modifications, but in the same time presents a porosity high enough to be permeable.

The porous nickel supports studied by mercury porosimetry had a total porosity of 29.45 % and an average pore diameter of 4.08 µm in case of the samples made of spherical powder and a total porosity of 34,47 % and an average pore diameter of 4,61 µm in the case of the samples made of irregular powder.

The tortuosity was 3,5 for the samples made of irregular powders and 1,7 for the samples made of spherical powders.

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Suporturi poroși de Ni pentru membrane de filme subțiri

Rezumat: Celulele de combustie depuse pe suport metalic sunt promițătoare datorită proprietăților mecanice și termice foarte bune. Oțelurile inoxidabile sunt foarte des utilizate pentru realizarea suporturilor. În acest studiu au fost efectuate încercări privind utilizarea pulberilor de Ni pentru realizarea unor suporturi poroși. S-au folosit pulberi sferice de Ni (de puritate 99.8% Ni) cu granulația cuprinsă între 5 și 15 μm și pulberi neregulate de Ni (de puritate 99.99% Ni) de granulație sub 6 μm. Suportii poroși din Ni au fost realizați prin presarea uniaxială a pulberilor la 400 MPa, sinterizarea a fost făcută în vid (10^{-5} Torr) la 550 °C. Durata de menținere la temperatură a fost de 60 de minute pentru a obține porozitatea deschisă necesară. Probele sinterizate au fost studiate prin SEM și porozimetrie cu mercur.

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