

CREATION OF HYDROGEN - SELECTIVE TUBULAR COMPOSITE MEMBRANES BASED ON PD-ALLOYS: PREPARATION OF CERAMIC SUPPORT

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Introduction

Application of homogeneous dense metal membranes based on Pd-containing alloys allows effective production of high-purity hydrogen from various technological gases. Perspective alternative to these expensive membranes (with thickness not less than 50 μm) is development of composite membranes with porous supports allowing considerable reduction of Pd layer thickness and membrane cost and ensuring at the same time enhanced permeability and good operating ability. The main problem here is to prepare supports with such porous structure which, first, would allow to produce defect-free thin selective Pd - containing layer; and, second, have good performance property and transport parameters in hydrogen media at high temperature. And finally, cost of such supports should be significantly lower than that of traditionally used Pd – alloy foils with thickness of 50 micron. According to estimates the mean pore diameter in the support surface layer should be less than

0.05 micron. Therefore commercially available porous materials can not be directly applicable.

Hence for creation of high-temperature composite membrane with Pd – based selective layer it is necessary to select supports satisfying necessary working conditions and to modify the surface for finishing deposition of thin selective Pd-alloy layer.

Results and discussion

The possibility of preparation of support suitable for hydrogen permselective composite membrane has been studied in this work. Manufactured in Russia (TU - 3113-001-001739 01-95) mesoporous ceramic $\alpha\text{-Al}_2\text{O}_3$ - tubes with the outer diameter of 8 mm have been used as porous substrate. They have high thermal and chemical stability, mechanical strength and durability. Tubular shape of support compared to the flat one provides effective membrane sealing, higher packing density in the apparatus and

enhanced thermal stability of the barrier layer. Mean pore diameter in the barrier layer of these tubes is 0.2 micron. Porous structure of the outer support surface has been modified by deposition of the additional layer of metal Ni. Nickel, as well as palladium, is excellent catalyst of molecular hydrogen dissociation, and therefore it would compensate decrease in effective cross section of surface pores especially at temperature rising (see the Table presenting some hydrogen diffusion parameters in nickel and palladium known from the literature).

Metal	$t, ^\circ\text{C}$	$D_0, \text{cm}^2/\text{s}$	$Q_{\text{act}}, \text{kJ/mole}$
Ni	336-1400	6.9×10^{-3}	40.5
	125-1325	7.85×10^{-3}	40.8
	180-430	5.18×10^{-3}	40.0
Pd	0-650	6.0×10^{-3}	24.5
	-77-725	2.9×10^{-3}	22.2

Two vacuum condensation techniques have been used for nickel deposition: ion magnetron sputtering and electron beam evaporation. These techniques enable to produce coatings as thin films of high purity and practically any composition on various supports including porous ones. Several recent publications underline that use of vacuum deposition techniques, especially magnetron sputtering, is very perspective for development of ceramic based membranes.

Structure, morphology and other properties of the deposited coatings have been investigated by means of scanning electron microscopy (S-570, Hitachi), X-ray diffraction measurements using $\text{Cu K}\alpha$ radiation, gas permeability testing and bubble point method.

Ni peaks at $2\theta = 44.5^\circ$ and $2\theta = 51.9^\circ$ can be seen on X-ray patterns of the samples obtained by the both vacuum deposition techniques (Fig.1). They correspond to ASTM data 4-850 for Ni (peak $2\theta = 44.5^\circ$ (111), $I/I_0 = 100$ and $2\theta = 51.9^\circ$ (200), $I/I_0 = 42$). Weak peaks of the ceramic support are

also seen. Ni peaks for the case of electron beam evaporation are sharper, crystallinity of the coating is higher compared to the magnetron sputtering case. Sputtered coating is more dispersed.

This is also confirmed by SEM of top surfaces of nickel coatings obtained by magnetron sputtering (Photo 2) and by electron beam evaporation (Photo 3) and by results of gas permeability testing using air and bubble point study. Structures formed due to coating deposition significantly reduce support permeability not only due to mean pore diameter decrease but also due to decrease in the total cross section of surface pores.

Conclusions

Tubular composite α -Al₂O₃ -based supports for Pd-containing metal membrane have been developed. Their distinction consists in using metal nickel for the modification of the porous structure of ceramic substrates. Nickel is analog of palladium in many respects, it is also effective catalyst for molecular hydrogen dissociation. Comparative analysis of two vacuum condensation methods, magnetron sputtering and electron beam evaporation, used for nickel deposition has been carried out.

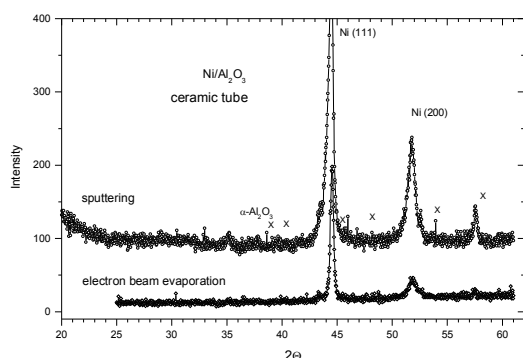


Fig. 1. XRD patterns of Ni-coated samples.



Photo 2. SEM of Ni/ α -Al₂O₃ membrane. Top surface of nickel coating obtained by magnetron sputtering.

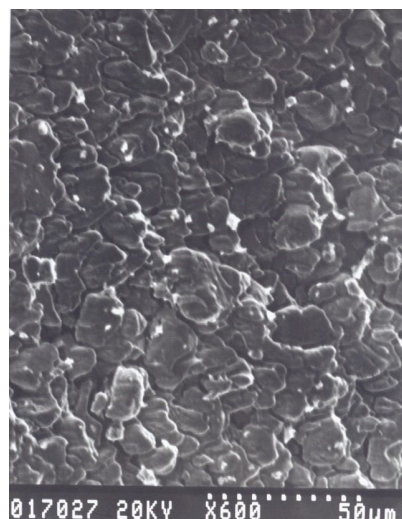


Photo 3. SEM of Ni/ α -Al₂O₃ membrane. Top surface of nickel coating obtained by electron beam evaporation.