


國立交通大學
材料科學與工程研究所

博士論文

電鍍法在不銹鋼載體製備鈀膜與其在氫氣純化及滲透的應用

Preparation of electroplated palladium membrane on the porous stainless steel
substrate and its applications in hydrogen purification and permeation.



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中華民國九十七年八月

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Submitted to Department of Materials Science and Engineering

College of Engineering

National Chiao Tung University

In Partial Fulfillment of the Requirements

For the Degree of Doctor of Science

In Materials Science and Engineering

Hsinchu, Taiwan, Republic of China

中華民國九十七年八月

中文摘要

有關鈀膜之製備，目前已知技術係以無電鍍法 (electroless)、真空濺鍍 (sputtering)、或冷軋法 (cold-rolled) 來進行。其中，有關在多孔性金屬載體上的鈀膜覆鍍，目前皆採用無電鍍法製程，然而，無電鍍法係依賴化學還原後金屬微粒在基材上的物理吸附而附著鍍膜，鍍膜與多孔性金屬載體間的附著力不強，故所製備的鈀膜常在使用一段時間後，因鈀膜與載體熱膨脹係的差異，鈀膜會從多孔性金屬載體上剝離。本研究成功以電鍍的方式於多孔性金屬載體上提供高附著性之鈀膜，可用於提供氫氣純化或合成用之觸媒反應器的鈀膜管件。

本論文係欲研究於多孔性不銹鋼載體上電鍍鈀膜，並探討氫氣滲透電鍍鈀膜之行為，論文架構包含三個主題，分別為

1. 多孔性不銹鋼表面前處理。
2. 電鍍鈀膜之備製。
3. 氫氣滲透電鍍鈀膜行為研究。

首先針對 AISI 316L 多孔不銹鋼於 60~80°C 的 1:1、2:1 以及 3:1 磷硫酸混合液進行電解拋光研究。電解拋光的拋光電位選定在陽極極化曲線中平坦的極限電流區，並搭配旋轉圓柱電極系統 (RCE) 進行測試。由結果可以得知混合液的比例與拋光溫度對於多孔不銹鋼有顯著的影響。最佳的表面整平與亮化效果的條件是在 70°C 的 2:1 的混合液。然而 1:1 和 2:1 混合液的溫度若是超過 75°C，則 PSS 表面的孔洞就會明顯的擴大，推測其原因可能是在孔洞內快速的解離所

致。此外在 3:1 的混合液中隨著溫度的變化 (60~80°C)，PSS 表面會有不同的形貌產生。但 PSS 形貌均具有圓角化的情況發生。所有的混合液比例與拋光溫度對於 PSS 的影響均利用電化學測試設備進行測試，而 PSS 表面形貌的變化則利用掃瞄式電子顯微鏡來進行觀察與輔證。

接著，已經成功地利用旋轉圓柱電極系統在 PSS 表面以電鍍的方式備製鈀膜，在電鍍的過程中，使用高轉速以及低電流密度可以有效地減少氫氣的共沈積，得到表面平整且無缺陷的鈀膜。藉由電鍍所備製的鈀膜對於氫氣滲透特性，如氫氣流量與選擇率($H_2/He > 100,000$)等均有不錯的表現。在甲醇重組反應中，電鍍鈀膜由混和氫氣中粹取之氫氣純度亦相當優異 (4N8)。此外由結果發現電鍍鈀膜在 250-350°C 的相變化溫度區間中，當氫氣壓力為 9kgf/cm^2 時電鍍鈀膜並無產生氫脆的現象，因此推測電鍍鈀膜對於氫脆有較佳的抵抗性。

最後針對 $H_2 + Y$ 的混和氫氣透過鈀膜的滲透行為，利用新式的定濃度方式來進行研究。定濃度法乃為解決氫氣混合氣體進行氫氣滲透鈀膜實驗時，引發氫氣濃度遞減效應所創建氫氣滲透鈀膜的實驗方式。由實驗結果得知，混和的氫氣的滲透性與純氫的滲透行為截然不同。由 Sievert's equation $Q = J_H / [(P_R^H)^{1/2} - (P_P^H)^{1/2}]$ ，即使調整了氫氣的分壓也無法得到正確的氫氣流量與滲透量，而混和氫氣中的氫氣濃度也會影響到氫氣的流量與滲透量。

雖然鈀膜只容許氫氣滲透，不使其他氣體滲透通過(如氮氣、氬氣或甲烷)，但在氫氣滲透現象存在下少量的其他氣體都會與氫氣一同滲透過鈀膜造成滲透端氫氣純度的低落，即使鈀膜並無缺陷存在此一現

象依舊存在，此為一種新現象，文獻中尚無記錄。造成這種滲透的原因歸咎於鈀晶格在吸附氫氣後的伸縮性膨脹造成晶格間孔隙的放大。

研究結果將以掃描式電子顯鏡、穿透式電子顯鏡、X-ray 能譜分析儀、電化學檢測技術以及氣相層析儀，來觀察並探討電鍍鈀膜與氫氣滲透之影響。



English abstract

In this thesis, a novel palladium membrane electroplated on porous stainless steel support was developed for hydrogen separation process. Also the performance of the as-developed Pd- membrane was studied. The thesis is reported sequentially in three sections as follows:

First, the electrochemical polishing of porous stainless steel (PSS), AISI 316L, in the phosphoric-sulfuric mixed acid with a volume-ratios of 1 : 1, 2 : 1 and 3 : 1 at temperatures ranging from 60°C to 80°C was studied. Electrochemical polishing of PSS was performed in the potential located in the limiting-current plateau of its anodic polarization curve using a rotating cylinder electrode (RCE). The results show that the electrochemical polishing of PSS is strongly affected by the volume ratio of the mixed acid and the polishing temperature. An optimal brightening and leveling surface of PSS could be achieved by polishing in 2 : 1 v/v mixed acid at 70°C. Whereas, polishing in 1 : 1 and 2 : 1 v/v ratios at and above 75°C would result in formation of enlarged pores on the PASS surface due to high dissolution rate within the pores. There is difference in the surface morphology of PSS when polishing in 3 : 1 v/v mixed acid at temperature range from 60°C to 80°C, but with rounded edges around the surface pores of PSS. The effect of the acid volume-ratio and the polishing temperatures on polishing PSS was discussed based on the results of electrochemical test and the observed polishing surface morphology using scanning electron microscope (SEM).

Secondly, a novel electroplating method of preparing Pd membrane on an AISI 316L porous stainless steel support is successfully developed

by proper control of rotation speed of the support. The use of low current density with high rotation speed enables us to avoid hydrogen absorption during electroplating and to prepare smooth thin membrane with defect-free. The electroplated-Pd membrane shows well property in the hydrogen permeation, flux and excellent permselectivity($H_2/He > 100,000$), the Pd membrane is used in a steam reformer of methanol for the production of high purity hydrogen. It was also found that the membrane spontaneously exhibited resistance to hydrogen embrittlement around the phase transition temperature of 280°C , when operated in the temperature range of 250°C - 350°C under the hydrogen pressure of 9kgf/cm^2 .

Finally, the newly developed constant concentration method was adopted to study the hydrogen permeation of a hydrogen mixture of $H_2 + Y$ through a palladium membrane tube. The hydrogen permeation of the hydrogen mixture differs from that of a single hydrogen feed. For the hydrogen mixture, the well known Sieverts equation, $Q = J_H / [(P_R^{H_2})^{1/2} - (P_P^{H_2})^{1/2}]$, fails to yield the correct hydrogen flux or permeance even after the pressure terms are adjusted to the partial pressure of hydrogen. The hydrogen concentration in the mixture affects both the flux and the permeance.

Significant abnormal permeation of the non-hydrogen gas, Y, in the hydrogen permeates is detected during the hydrogen permeation of the mixture, $H_2 + Y$, even though Y-gas alone does not permeate through the defect-free palladium membrane. This Y-gas slippage in the presence of hydrogen in the mixture is tentatively attributed to the expansion of the palladium atomic lattice, enlarging inter-cluster openings Y-gas permeates through the enlarged structure or grain boundary of the palladium atoms in the membrane.

誌 謝

本論文得以之完成，首先要感謝所內各位師長的指導，尤其指導教授涂肇嘉博士及雷敏宏博士，多年來的鼓勵、支持與幫助，讓我獲益良多，非千言萬語可表示我誠摯的感激。感謝碧氫科技開發股份有限公司於經費上的全力協助，使本研究可順利無礙的進行，並感謝口試委員台灣大學吳紀聖博士、系上的朝春光博士與吳樸偉博士在百忙之中抽空給予學生論文上的建議與指導，口試時的指導及思考方向的指引，使我受益良多，不勝感激。另感激長庚大學機械系王能治博士、黃清安博士、張耀仁博士、孫明宗博士、蔡明義博士、林忠男先生、劉朝陽先生、謝天揚先生與洪慧文小姐等人在學術、技術和儀器操作上給予支援，還要謝謝材料系辦公室內熱忱的工作人員在各項事物的提醒與幫助。感謝林文學長與高玉玲學姐在漫長的求學過程中不斷的勉勵與打氣，同時也要感謝交大實驗室的學弟林勝結與謝逸凡謝謝你們給予我最大的幫助，藉此成果與您們分享。論文的完成，感謝碧氫科技的同仁洪嘉業、汪杭甫、葉冠廷、蔡易秀與楊勝淵在研究中給予許多協助。感謝同窗好友以及學弟妹們，有你們大家的陪伴，使我研究生時期多采多姿。

僅以此論文獻給愛我的家人及女友婉庭。感謝你們的支持，學習旅程中你們的陪伴與付出使我勇敢、增我信心，使我無後顧之憂得以順利完成學業而有此著作，願以此著作與你們分享。

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