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# PREPARATION AND CHARACTERIZATION OF Pd AND Pd–Ni ALLOY MEMBRANES ON POROUS SUBSTRATES BY MOCVD WITH MIXED METAL β-DIKETONE PRECURSORS

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## ABSTRACT

A novel metal-organic chemical vapor deposition(MOCVD) process with a mixed metal  $\beta$ -diketone precursor to successfully prepare Pd and Pd-Ni alloy composite membranes is described. A palladium phase deposit consisting of agglomerates of tiny crystallites with a dimension of around 30 ×10 nm was formed on porous Al<sub>2</sub>O<sub>3</sub> substrates, when using a single Pd(AcAc)<sub>2</sub> precursor. With a mixed precursor of Pd(AcAc)<sub>2</sub> + Ni(AcAc)<sub>2</sub>, uniform and dense Pd-Ni alloy membranes (consisting of primary crystallites with a dimension of 40 × 15 nm) were reproducibly obtained on porous alumina supports. N<sub>2</sub> permeation tests indicated that the Pd-Ni alloy layer was gastight and crack-free. XPS studies revealed that no oxygen nor carbon impurities were incorporated into the bulk membranes. The Pd/Ni ratio on the surface of Pd-Ni alloy layer was very close to that of the mixed precursor, but much less Ni content (<1/150) was detected in the deposit body. *Copyright* C 1997 Elsevier Science Ltd

KEYWORDS: A. alloy, A. composites, A. organometallic compounds, A. thin films, C. vapor deposition

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### **INTRODUCTION**

Palladium and Pd-based alloy thin films have found wide applications in the areas of electronics, gas sensors, hydrogen purifiers, magnetic storage devices, etc. [1]. In particular, there has been considerable research activity in the development of Pd-based alloys for use as a membrane material for high temperature gas separation and hydrogen permeable membrane reactors, because of their highly hydrogen permeselectivity and catalytic properties. For this purpose, the key requirements on Pd or Pd-based alloy membranes are good thermal stability, sufficient mechanical strength, as well as high hydrogen permeation flux.

Conventional processing technique, such as cold rolling, can only provide Pd or Pd-based alloys sheets with a minimum thickness of around 100  $\mu$ m. This thickness is still too large to obtain the desired hydrogen permeation flux. In addition, the poor mechanical properties due to hydrogen embrittlement is also a severe barrier for their usage as membrane materials. One way to overcome these obstacles is to make composite membranes which consist of thin Pd or Pd-based alloy membranes deposited on the surface or inside of a strong porous substrate [2]. Techniques such as physical vapor deposition (PVD) [3], electroless-plating [4], and chemical vapor deposition (CVD) [5] have been attempted for the fabrication of Pd and Pd-based alloy composite membranes. PVD can only result in a top layer on the surface, as the physical vapor does not penetrate the porous substrate. The adhesion of such a membrane can be poor and the hydrogen embrittlement cannot be avoided completely. Electroless-plating is based on the deposition from liquid solution; hence, it is very difficult to obtain a thin dense membrane. Compared with these techniques, CVD processes exhibit distinct advantages: (1) Very thin membranes can be obtained because of its molecular level



FIG. 1 Schematic diagram of the MOCVD apparatus for multi-component compound thin films.

growth mechanism, and (2) using counter-diffusion CVD, functional materials can be grown inside the pores of the support, so that the improved mechanical property with ultrathin membrane, hence large hydrogen permeation flux, can be expected [6]. However, the precursors for CVD techniques of Pd and its alloys have been a problem. The precursors for CVD should have sufficient vapor pressure or sublimation ability as well as good thermal stability at temperatures lower than that for film deposition. PdCl<sub>2</sub> was attempted as precursor, but PdCl<sub>2</sub> exhibits poor sublimation ability until temperatures as high as 300–500°C, at which PdCl<sub>2</sub> decomposes considerably. Therefore, it is difficult to control the CVD process in order to obtain desired dense membrane [7]. MOCVD with metal  $\beta$ -diketone chelates as precursors has been successfully developed to prepare high T<sub>c</sub> superconducting oxide YBaCuO [8] and YSZ [9] thin films. Furthermore, a novel mixed precursor technique for MOCVD with  $\beta$ -diketone chelates has been demonstrated to have advantages in composition, and hence property control, for the preparation of multi-component thin films [10,11].

In this work, we present the successful combination of this novel MOCVD with counter-diffusion CVD process to make Pd and Pd-Ni composite membranes on porous ceramic supports.

#### EXPERIMENTAL

The MOCVD apparatus, as schematically shown in Figure 1, consists of three parts: precursor supply device, deposition reactor, and vacuum system. The precursor supply is conducted by a mixed precursor technique which was described in detail for  $YBa_2Cu_3O_{7-x}$  superconducting oxide thin films by Meng et al. [10]. In this work, either  $Pd(AcAc)_2$  for a palladium membrane or  $Pd(AcAc)_2 + Ni(AcAc)_2$  mixture for a Pd–Ni alloy membrane was made compact in a glass tube with a slot for precursor evaporation. The tube was moved by a magnet carrier into the heating zone, where the ß-diketone chelates were sublimated into the vapor phase under the radiation of a halogen lamp. Argon was used as carrier gas to transport the precursor vapors into the deposition reactor, and the reducing agent H<sub>2</sub> was inlet from the other side of the porous substrate, which allowed the deposition reaction to take place through the so-called counter-diffusion CVD process:

Precursor vapor (top side) +  $H_2$  (bottom side) = Pd-Ni/support + [C.H] +  $H_2O$ 

Porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> disks and porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> disks coated with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> top layer by a solgel process were employed as the supports. The pore sizes of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layers were 150 and 4 nm, respectively. The typical deposition parameters were as follows:

0.8 mm/min
6080 V
80-100 SCCM
$(1-1.5) \times 10^3$ Pa
350-400°C
100 min

X-ray diffraction (XRD) technique was used to identify the phase of the deposit. Both surface and fracture morphology of Pd and Pd–Ni membranes were investigated by scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) was employed to study the layer composition. The gastight property of the specimens was examined by  $N_2$  permeation measurement.



XRD patterns of Pd and Pd–Ni alloys deposited on porous alumina substrates: (a) Pd on porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>; (b) Pd–Ni on porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.









(c)

FIG. 3

SEM photographs of a Pd layer on porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support: (a) as-deposited surface of Pd layer; (b) fracture morphology of Pd layer; and (c) after annealing at 500°C in vacuum.

## **RESULTS AND DISCUSSIONS**

**XRD Identification.** XRD patterns (Fig. 2a) indicate that a fcc Pd film was formed on the porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate when using single Pd(AcAc)<sub>2</sub> precursor. The crystallite sizes estimated from the peak broadening of Pd(111) and Pd(220) are 28.2 and 10.4 nm, respectively. With a mixture of Pd(AcAc)<sub>2</sub> and Ni(AcAc)<sub>2</sub> in a Pd/Ni ratio of 92/8, the Pd-Ni membrane obtained exhibits a single fcc phase (Fig. 2b) as pure Pd layer, but the peaks are sharper. This demonstrated the formation of Pd-Ni alloys with better crystallinity. The primary particle sizes estimated from the Pd(111) and Pd(220) peaks are 38.5 and 15.4 nm, respectively. This implies that incorporation of Ni atoms into Pd fcc phase does not much influence the crystal lattice, as expected from the Pd-Ni phase diagram which shows

unlimited solid solubility. However, this results shows that the existence of Ni atoms affects the film growth behavior.

Membrane Morphology. Figure 3 presents SEM micrographs of Pd composite membranes. The pure Pd film consists of deposit particles (Fig. 3a) in diameter of about 1 µm, which are clearly agglomerates of very tiny Pd primary crystallites in spindle shapes. The sizes of the primary crystallites are obviously smaller than 100 nm, which is consistent with the results obtained from XRD. The thickness of the deposit layer is approximately 1 µm (Fig. 3b) which is close to the size of the agglomerates. This may be related to the pore size of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate. Fig. 3c shows the surface morphology of the sample after annealing at 550°C in vacuum. It appears that the agglomerates became sintered grains and the contact between each other is much improved, but the membrane remains porous.



**(a)** 





FIG. 4

SEM photographs of Pd–Ni alloy membrane supported on porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>: (a) surface; (b) fracture; (c) element (Pd) line scan analysis.

The Pd-Ni alloy layers are smooth and dense, as shown in Figure 4. Figure 4a shows that the membrane consists of very fine grains in spindle shape with dimensions of less than 100 nm. This observation is quite consistent with the primary crystallite sizes estimated from XRD. From the fracture micrograph (Fig. 4b) the layer has a good coherency to substrate and the thickness is estimated to be 4  $\mu$ m. Some isolated particles which have been identified as Pd by the line scanning element analysis (Fig. 4c) are present on the surface and are supposed to have formed by post-nucleation and growth.

Membrane Compositions by XPS. To determine whether in the membranes there is incorporation of impurities, such as carbon and oxygen, which are contained in the metal  $\beta$ -diketone precursors, the sample surface was investigated by XPS. According to the XPS results, the surface of as-deposited membrane contains mainly Pd and Ni; small peaks related to oxygen and carbon also were observed (Fig. 5a). A narrow region scan of Pd(3d) peaks (Fig. 5b) shows shoulder peaks clearly due to the oxidation of palladium. But after removal of a layer of less than 10 nm by Ar+ sputtering, the Auger peak for oxygen, O(KVV) as well as the shoulder peaks of Pd(3d) completely disappeared (Fig. 5c and d), and the C<sub>1s</sub> peak of carbon became very weak. Thus, the membrane contained less than 0.1 atom% oxygen or carbon impurities. The XPS peaks of carbon and oxygen peaks which appeared at the surface of as-deposited layer can be attributed to contamination from the system environment. The H<sub>2</sub> reactant can exclude the impurity incorporation by forming H<sub>2</sub>O and hydrogen carbon compounds.

The XPS peak intensity for Ni decreased to zero after removal of the surface layer by Ar+ sputtering (<10 nm). The Pd:Ni ratio on the surface of as-deposited membrane was estimated from the corresponding XPS peaks to be 92:8, which is very close to the Pd:Ni ratio in the mixed precursor. After removal of the surface layer by Ar+ sputtering, the Pd:Ni ratio became 153:1. This suggests that the existence of Ni atoms adsorbed on the growing surface considerably influences nucleation and growth behavior, leading to a much improved uniform and dense membrane.

 $N_2$  Permeation Testing. Figure 6 presents the results of the  $N_2$  permeation for Pd and Pd-Ni membranes on porous Al<sub>2</sub>O<sub>3</sub> support. No  $N_2$  permeation was detected for the Pd-Ni alloy membrane up to an average pressure of 0.3 MPa, indicating that fully dense Pd-Ni membranes have been obtained using this novel MOCVD technique. This is of great significance for use as hydrogen permeable membrane in gas separation and membrane rectors for dehydrogenation and hydrogenation reactions. A study on hydrogen permeation at elevated temperatures is underway.

 $N_2$  permeation flux of the Pd membrane prepared with single Pd(AcAc)<sub>2</sub> increases linearly with the mean pressure, indicating the presence of pinholes and cracks. However, the slope of the permeation flux versus mean pressure curve is considerably smaller than that for porous support.

## CONCLUSIONS

A novel MOCVD technique with  $\beta$ -diketone precursors, Pd(AcAc)<sub>2</sub> and Ni(AcAc)<sub>2</sub> has been successfully developed to prepare Pd and Pd–Ni alloy thin layers on porous Al<sub>2</sub>O<sub>3</sub> ceramic substrates. Both Pd and Pd–Ni alloy layers exhibit the fcc phase without oxygen and carbon





XPS spectra of Pd-Ni membrane on porous alumina: (a) survey scan of as-deposited membrane; (b) narrow region scan for Pd (3d) peaks on as-deposited Pd-Ni membrane sample; (c) survey scan of the sample after removal of surface layer by Ar+ sputtering; (d) narrow region scan for P (3d) peaks on the sample after removal of surface layer by Ar+ sputtering.



FIG. 5 Continued



FIG. 6

N<sub>2</sub> permeance of the Pd and Pd-Ni composite membranes versus mean pressure. ( $\Box$ ) porous  $\alpha$ -alumina support; ( $\Delta$ ) Pd layer deposited using Pd(AcAc)<sub>2</sub> precursor; ( $\blacktriangle$ ) Pd-Ni alloy using Pd(AcAc)<sub>2</sub> + Ni(AcAc)<sub>2</sub> precursors.

impurity incorporation. The primary crystallites are spindle shape with the dimensions  $15 \times 40$  nm and  $10 \times 30$  nm for Pd and Pd-Ni alloy deposits, respectively.

Mirror-like and dense membranes on porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate can be reproducibly obtained when using a mixture of Pd(AcAc)<sub>2</sub> and Ni(AcAc)<sub>2</sub> precursor. The membranes are gastight and free from pinholes and cracks as indicated by the near constancy of N<sub>2</sub> permeance with the variation of the mean pressure applied.

In the case of using only  $Pd(AcAc)_2$  to deposit Pd membranes, it appears that the layer consists of agglomerates and is not gastight. This implies quite a different growth mechanism in the existence of Ni(g), which is worth further study.

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