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# **Noble metal membrane preparation: Industrial film formation techniques**

**Work package 1.2.F1 Hydrogen  
Membrane Technologies CATO2A**

## **Deliverable 2**

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## Abstract

This report describes in a generic way industrial techniques suitable for formation of (noble) metal films with the aim of preparation of palladium based hydrogen separation membranes on a large scale. Industrial film formation techniques are used in many other industries, like semiconductors, laminated foil industry, metal/plastics industries etc. The aim is finding promising industrial film formation or deposition techniques or routes that can be used for the manufacture of palladium or palladium alloy membranes.

Input for this report is collected from available literature and private communications with several companies that are active in the foil/film production. A list of requirements that has to be met for the palladium/palladium alloy films/foils is cross checked with large scale manufacture techniques.

It was concluded that vacuum techniques, in particular sputtering, are the most versatile and promising techniques for the direct deposition of binary, ternary, multicomponent palladium alloys on porous substrates.

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## Executive Summary

Inorganic palladium alloy based hydrogen selective membranes on porous tubular supports are among others one of the more promising techniques for separation of hydrogen from gas mixtures.

The performance, flux, selectivity, longevity, of the Pd-alloy membranes is highly dependent on the alloy composition and thickness. Current commercial available Pd-based membranes in the form of foils and tubes have a relatively thick Pd layer ( $> 20 \mu\text{m}$ ). There is a trend towards the preparation of thinner Pd-based membrane to reduce costs and increase flux. Several techniques can be used for the preparation of thin film ( $< 5 \mu\text{m}$ ) Pd-based membranes on a small scale in laboratories. In case of film thinner than 10 micron mechanical strength is provided by a porous support.

The primary objective of this report was to find and compare promising industrial film deposition or film formation processes that are suitable for manufacturing thin film Pd-alloy membranes on porous tubular supports on a large scale. The envisioned length scale of the porous tubular supports is in the order of meters. Several requirements have to be met by the industrial film formation techniques. The more important requirements for Pd-alloy membrane production technologies are: applicability to porous (tubular) supports, flexibility in the controlled formation of Pd-alloy of two or more alloying components and capabilities of depositing on large areas without defects. Industrial film formation techniques are used in many other industries, like semiconductors, laminated foil industry, metal/plastics industries etc. Information is collected from available literature and private communications with several companies, industrial contacts and scientific research groups that are active in the foil/film production. This report summarizes public information and does not claim to fully cover all data with respect to industrial film formation techniques.

The report evaluates industrial techniques suitable for formation of (noble) metal films with the aim of preparation of Pd based hydrogen separation membranes on a large scale. The list of requirements that has to be met for the Pd / Pd-based alloy films/foils is cross checked with the characteristics and properties of the large scale thin film manufacture techniques. The promising industrial film formation techniques that were identified are: film blowing, rolling, atomic layer deposition, tube drawing, chemical thinning, laser assisted deposition, pulsed layer deposition, thermal spraying, electroless plating, electro deposition, chemical vapor based deposition and physical vapor based deposition techniques.

The following conclusions can be drawn based on the findings of this report:

- Vacuum (low pressure) techniques based on physical vapor deposition (PVD) in particular sputtering, are the most versatile techniques for the direct deposition of binary, ternary, multicomponent Pd-alloys on porous substrates.
- The chemical thinning process is at the moment limited in its applications to PdCu foils.
- Rolling of thin foils is limited due to the pinhole formation at reduced foil thickness ( $< 6 \mu\text{m}$ ). There is also a risk for the formation of brittle intermetallic phases in the Pd-alloy at a certain chemical composition. At the moment there is a limited amount of data on the mechanical flow behavior of multicomponent (more than 4 elements) Pd-alloys during rolling.
- Film blowing extrusions of foil techniques for polymer based material are not suitable. This technique is not suitable for metals due to differences in mechanical/flow behaviour of the metals.

- Atomic layer deposition (ALD) and Fast-ALD are also rejected as a suitable technique because of the very low layer growth rate.
- Chemical vapour deposition techniques are also rejected because there is a limited amount of feasible mostly highly toxic precursors for the deposition of Pd-alloys.
- Deposition techniques using dissolved reactants like electroless and electro deposition are less suitable for the production of binary, ternary and multicomponent Pd-alloys due to difficulties in controlling the alloy composition and layer thickness on large areas. Electrodeposition is in principle only limited to electrical conducting supports.
- Thermal spraying is no option due the relatively high thickness of  $> 50 \mu\text{m}$  that is required in order to manufacture defect free films.
- Drawing of thin walled tubes is no option for the manufacturing due to the unfavourable tube diameter to membrane thickness ratio. It is impossible to manufacture a thin walled ( $< 5 \mu\text{m}$ ) Pd-alloy tube with a internal diameter of 1.5 cm.
- Laser assisted processing can not be used for the deposition of Pd-alloys on large areas at the moment. This is due to the formation of relatively thick porous layers.
- Pulsed layer deposition is not a suitable technique because of the limitation in substrate size of and the limitations in up-scaling of this process.

It is recommended to continue a closer investigation of sputtering techniques. Special attention have to be paid to parameters such as: temperature, pressure, comparison of 2-D sputtering configuration (x-y substrate or target movement) versus 3-D (x-y-z substrate or target movement) sputtering configuration on the deposited Pd-alloy layers on porous substrates.

## 1. Introduction

This report describes in a generic way industrial techniques suitable for formation of (noble) metal films with the aim of preparation of palladium based hydrogen separation membranes on a large scale.

A literature review done by (Exter, 2009) describes alternative deposition techniques for the current ECN deposition techniques and is mainly based on state of the art within the membrane/fuel cell/H<sub>2</sub> research community.

Industrial film formation techniques are used in many other industries, like semiconductors, laminated foil industry, metal/plastics industries etc. The aim is finding promising industrial film formation or deposition techniques or routes that can be used for the manufacture of palladium or palladium alloy membranes.

Input for this report is collected from available literature and private communications with several companies that are active in the foil/film production.

This report contains the following issues:

- requirements of the film formation process,
- generic summary industrial film formation techniques,
- evaluation of industrial techniques based on the requirements for hydrogen separation membranes,
- discussion in the form of a summary of the results and conclusions followed .

## 2. Requirements

There are several requirements that have to be met by the industrial film formation techniques. These requirements are described according to:

- technical/fundamental requirements,
- layer thickness:  $\approx 5\mu\text{m}$  (performance decrease linear function thickness) performance limit of membrane of defect geometry (thicker layer lower pinhole tendency),
- selectivity  $> 1000$  (i.e. (better than 100-200) 1000x more  $\text{H}_2$  than other gases/molecules),
- pinholes allowed (when selectivity is met),
- minimum  $\text{H}_2$  flux ( $> 10^{-6} \text{ mol/Pa}\cdot\text{s}\cdot\text{m}^2$ ),
- pressure range (absolute): 1-100 bar,
- operating temperature range: 300-800°C,
- application requirements:
  - alloying elements: Pd, Au, Cu, Mo, Gd, Zr and Ag,
  - Pd-only,
  - binary alloys: Pd-Ag, Pd-Cu,
  - ternary alloys,
  - multicomponent Pd alloys, having more than three alloying elements,
- substrates:
  - porous ceramics (porous 0.1 – 0.05  $\mu\text{m}$ ),
  - porous metal (stainless steel) (porous nm pores),
  - substrate geometry,
    - tube ( $\text{Ø}$  1.5 cm) (0.8 cm inner diameter  $\rightarrow$  tube thickness 2-3 mm),
    - length: maximum 3 m (length x circumference x  $5\mu\text{m}$  layer thickness: required amount of material),
- thickness of support (second order\*),
- preferably: covering of outer wall (instead of inner wall of tube) to be able to withstand the 50-100 bar pressure difference,
- considerations/boundary conditions:
  - (potential) industrial process:
    - reproducible,
    - geometry as described above,
    - estimated 10000  $\text{m}^2$ /membrane installation (order of magnitude),
- costs: second order,
- environmental/recycling impact: second order,
- include also generic/other industries as well. Report from Marcel covers especially the known techniques within the fuel cell/ $\text{H}_2$  research community, but now also covering other industries (e.g. semiconductor, laminated foil industry, steel/plastics industries).

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\* Note: "Second/(second) order" indicates non-leading aspects at this stage; they are not automatically taken into account now. However, if one already foresees/knows that major environmental/health/economic concerns might arise these have to be mentioned.

### 3. Industrial processes

Classically the equipment for the deposition of thin films can be classified into three categories:

- thin film deposition equipment for device research and development,
- prototype equipment for the study of new or established deposition processes,
- thin film production equipment for device manufacturing.

Research and development equipment requires often a high degree of flexibility in deposition parameters for accommodating a variety of substrates. High product throughput and a high degree of equipment automation are usually not required. This is not the case for manufacturing of thin films on a large scale.

In literature several industrial thin film processes were reviewed (Ohring, 2002, Seshan, 2002, Coombs jr, 2001, Eason, 2007). The more promising forming and deposition techniques for production of thin films or foils on a large scale are (Ohring 2002, Seshan, 2002, Coombs jr 2001, Eason 2007):

- foil formation,
- rolling processes,
- chemical thinning,
- deep drawing,
- caser assisted,
- thermal spray techniques,
- physical or chemical deposition techniques,
- electroless plating,
- electroplating,
- combinations of the techniques.

## 4. Traditional foil routes

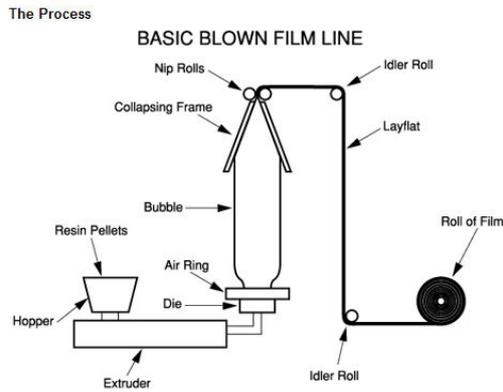
### 4.1 Packaging industry

Foils for packaging materials are often polymer based. Film blowing and foil extrusion are manufacturing processes for large scale polymer film and polymer foil production (Plasticstech, 2010). Blown film extrusion is the process by which most commodity and specialised plastic films are made for the packaging industry. The film blowing process basically consists of a extruding a tube of molten thermoplastic and continuously inflating it to several times initial diameter, to form a thin tubular product that can be used directly, or slit to form a flat film.

Plastic melt is extruded through an annular slit die, usually vertically, to form a thin walled tube. Air is introduced via a hole in the centre of the die to blow up the tube like a balloon. Mounted on top of the die, a high-speed air ring blows onto the hot film to cool it. The tube of film then continues upwards, continually cooling, until it passes through nip rolls where the tube is flattened to create what is known as a 'lay-flat' tube of film. This lay-flat or collapsed tube is then taken back down the extrusion 'tower' via more rollers. On higher output lines, the air inside the bubble is also exchanged. Figure 4.1 shows a schematic draw and a photo of the real scale process of the film blowing as an example.

Typically, the expansion ratio between die and blown tube of film would be 1.5 to 4 times the die diameter. The draw down between the melt wall thickness and the cooled film thickness occurs in both radial and longitudinal directions and is easily controlled by changing the volume of air inside the bubble and by altering the haul off speed. This gives blown film a better balance of properties than traditional cast or extruded film which is drawn down along the extrusion direction only.

No metal foils are made by this film blowing extrusion process, as far as could be found. One reason is that the mechanical behaviours of metal foils are from fundamental point of view completely different from that from polymer based materials.



(Plasticstech, 2010)

Schematic draw of the film blowing process



(Der Grüne Punkt – Duales System Deutschland GmbH, 2010)

Film blowing in real dimensions.

Figure 4.1 *Film blowing process*

## 4.2 Metal foil rolling

Metal foils can be made by classical ingot manufacturers followed by rolling to thin foils. Commercial production of aluminium foil is done on a large scale. Thin aluminium foils by Aleris, Alcan and Hydro are produced by a continuous casting process followed by hot rolling or cold rolling, Figure 4.2. This process bypasses the ingot stage and converts molten metal directly into a thick strip which is immediately rolled into the coil from which the foil is then rolled. To obtain the very thinnest foils, two layers are rolled simultaneously. This ‘double rolling’ results in the difference between the two surfaces – matt and polished – the matt side being the inner side during double rolling. In the doubling machine, a spray system injects a very thin film of rolling oil between the two foil layers. The oil acts as a separating medium or release agent to prevent cold-welding between the two metallic surfaces during rolling. The two layers of aluminium foil are then separated and heat treated and cleaned. Complete casting parameters for strip production on caster were defined and approved for alloys: AA 1050, AA 1200, AA 8011, AA 8079.

Virgin thin foils are expected to have pinholes. The pinholes can be caused by contaminants from the melting process, gas bubbles, lattice defects, from rolling debris and faults occurring during rolling foil production.

The table below shows allowable pinholes for different gauges of aluminium foils from one foil manufacturer. It is generally accepted that aluminium foils having thicknesses between 20  $\mu\text{m}$  and 25  $\mu\text{m}$  are pinhole free.

Pinholes form during rolling when the size of the fault is bigger than the thickness of the aluminium foil. The number of pinholes is increasing with decreasing foil thickness. Table 4.1 shows a typical pinhole count for aluminium foils of various thicknesses.

While few studies exist regarding the size distribution, inquiries with two foil vendors indicate that holes typically range in size from 10-50  $\mu\text{m}$  in diameter. Small holes tend to be circular, while the largest holes tend to be oval in shape, with dimensions up to 75  $\mu\text{m}$  by 200 $\mu\text{m}$  (Murray, 1998).

Table 4.1 *Pinhole counts for rolled thin aluminium foils (Murray, 1998)*

Foil thickness ( $\mu\text{m}$ )	Foil thickness (inch)	Pinhole (count/ $\text{m}^2$ )
6	0.00025	441
7	0.00030	215
9	0.00035	129
12	0.00050	64
18	0.00070	11
25	0.00100	0

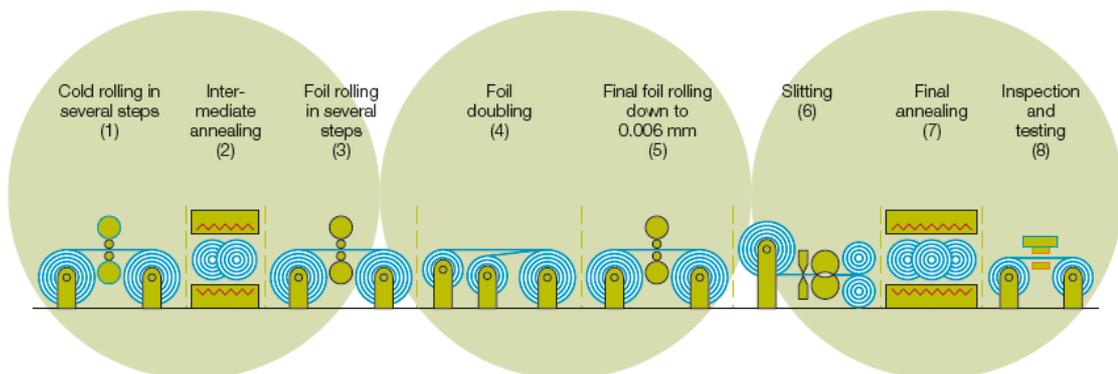


Figure 4.2 *Schematic draw of the double film rolling process from Hydro aluminium as used in Grevenbroich Germany (Hydro, 2008)*

The deformability of bcc crystallographic structures compared to fcc is lower and requires heat treatments between the deformation steps in order to lower the hardening. The manufacture of thin palladium foils with thicknesses of less than 50  $\mu\text{m}$  by rolling is theoretically cumbersome and cost-intensive because of the various rolling and intermediate annealing steps. In addition, the rolled foils with the smallest thicknesses can only be obtained with a maximum width of about 150 mm.

Foil thicknesses of 6  $\mu\text{m}$  are obtained by this method for aluminium alloys AA1050 and AA 1200 at a width of 1640 – 2040 mm (Hydro 2008). The key knowledge is in the precision rolling process. This requires knowledge on the flow properties of the rolled material as a function of thickness reduction. This is already done for several aluminium alloys. The reason for this is that there is a big market for applications of thin aluminium foils. At the moment this is not the case for palladium alloy foils. As a result there is no real push for technology development in the field of continuous rolling of palladium alloy foils with thicknesses in the range of 6  $\mu\text{m}$ .

In the past palladium thin metal membranes have been fabricated by rolling between precision rollers, but the potential for pinhole defects limits this method for palladium-alloy membranes to 25 microns (0.001 inch). Difficulty in controlling deformation across the length of the press

rolls used in forming the membranes limits the practical width of the membranes to approximately 10 cm. The key issue is developing the rolling technology of palladium alloy materials (Winde, 2010).

In order to overcome the issue of pinhole (defect) formation in palladium alloy membrane films over large areas, other processes were or have to be developed and implemented for producing 6  $\mu\text{m}$  to 12  $\mu\text{m}$  thick palladium alloy films and will be described below.

### 4.3 Foil thinning/chemical thinning

A possible route for the production of a palladium alloy foil is rolling of palladium alloy material to the minimum thickness that guarantees a pinhole free foil followed by another thinning step. Hy9 buys commercial available 25  $\mu\text{m}$  thick cold rolled palladium alloy foil. The foil is taken through a sequence of chemical etching steps that produces a defect-free membrane that is one half to a quarter of its original thickness (Lu, 2010)

Hy9 uses this method on a commercial base in which palladium-copper foil membranes are manufactured and reduced in thickness by chemical etching (US patent 6103028).

Figure 4.3 shows a palladium-copper foil before (left) and after (right) chemical thinning.

Although Hy9 claims that it produces well performing plate-frame membrane modules with this method, it is still questionable whether this is a so called cost effective method. Palladium and alloy components have to be removed from the etching baths and recovered.

An important key issue is finding a suitable chemical etching agent. Several etching agents for palladium are summarised in (Kaker, 2008). (Kaker, 2008) suggests also several etching agents for ternary palladium alloys in the element range of interest.

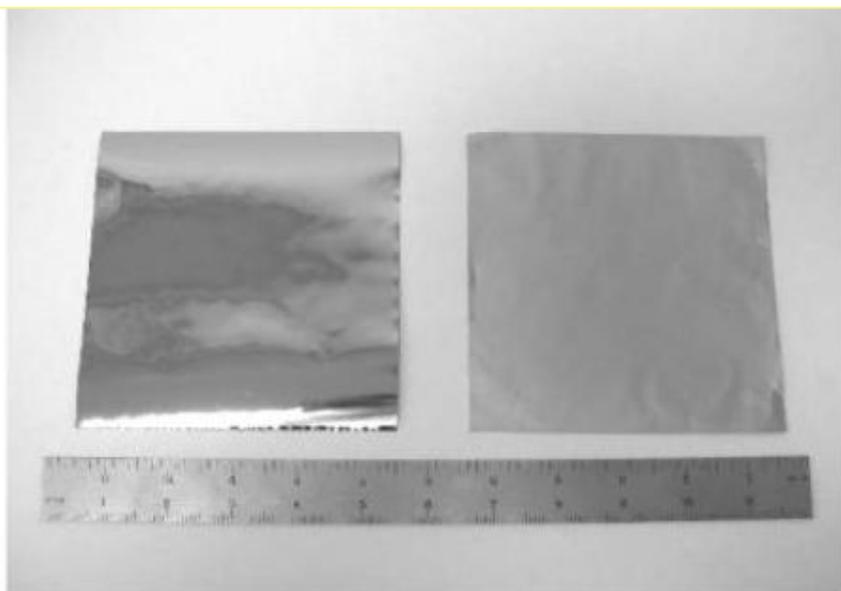


Figure 4.3 *Photographs of a 25  $\mu\text{m}$  thick rolled palladium-copper foil (left) and a 8  $\mu\text{m}$  thick palladium-copper foil after the chemical thinning process developed by Hy9 (right) (Lu, 2010)*

## 4.4 Joining metal foils

The manufacture of free standing palladium alloy films alone is not successful without suitable joining processes. Several welding and or soldering/brazing process can be used for joining of thin metal foils.

Private communications with Philips CFT and a former employee from Philips CFT on the subject joining of thin palladium alloy foils resulted in the following list of suitable joining techniques:

- Laser welding: is possible but will be very difficult for thin foils ( $< 5 \mu\text{m}$  thickness). This requires a narrow laser beam size in the order of  $< 10 \mu\text{m}$ . Another requirement is that the foils need to have a good contact such that no gap formation occurs. Sufficient clamping of pressure is required at the welding spot.
- Diffusion welding: The thermo-mechanical press was used to perform the thermal treatment under vacuum at a high temperature (approx.  $900^\circ\text{C}$  for 1 h). (Gallucci, 2007) used this method for joining a palladium foil around a tubular support F. (Gallucci, 2007) obtained a bonding via diffusion welding of a palladium-silver strip interposed between the palladium parts to be joined. This procedure is time consuming and requires a vacuum chamber. For these reasons this technique is often regarded as expensive.
- Resistance seam welding or roll welding: Two wheel-shaped electrodes roll along the foils. These electrodes apply a current and a pressure. Partial melting will occur at the contact interfaces resulting in an interconnection of the foils. A benefit compared to laser welding is that the heat input is relatively lower.
- Brazing or soldering: palladium alloys can be brazed with platinum. During this process the temperature is raised until platinum starts to melt. The liquid material spreads on the palladium alloy surface and results in a bond after cooling.

An example of a welded Pd-Ag membrane on a cylinder is shown in Figure 4.4.

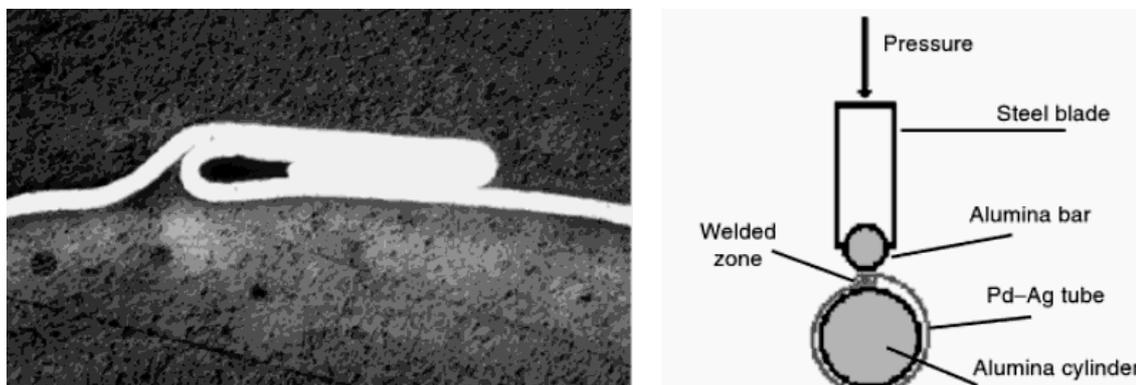


Figure 4.4 (left) Cross section of welded zone of a Pd-Ag alloy foil. (right) A schematic draw of the welding set-up for welding the membrane tubes (Mallada, 2008)

No further information was found on joining techniques for palladium foils.

## 4.5 Metal drawing/extrusion

The wall thickness of current standard palladium tubings is around  $100 \mu\text{m}$  thick (Johnson-Matthey, 2010). The maximum length can go up to three meters depending on the wall thickness. Advances in drawing thin walled metal tubes made it possible to manufacture palladium silver tubular membranes with a thickness of around  $20 \mu\text{m}$ . Smooth surfaces are

easily produced by foil rolling and seamless tube drawing. Palladium tubes with a wall thickness of 50  $\mu\text{m}$  and an outer diameter of 0.6 mm are available.

As a general rule irrespective of the composition of the metal alloy used, drawing thin walled ( $<100 \mu\text{m}$ ) is difficult and thus expensive if the diameter is 10 times or more the wall thickness. Based on general rule this and the lack of commercially available palladium tubes with a wall thickness of  $<5 \mu\text{m}$  with a diameter of 1.6 cm, it is concluded that deep drawing or extrusion is not an option as production route for thin walled tubular membranes.

## 5. Wet chemical

### 5.1 Electroplating

Plating is most commonly done with a single metallic element. Some alloys can be electrodeposited on commercial scale, like brass and solders.

A limitation in the commercial electroplating processes is related to the uniform thickness. Obtaining a uniform thickness with electroplating can be difficult depending on the geometry of the object being plated. The plating metal is preferentially attracted to external corners and protrusions, but unattracted to internal corners and recesses. These difficulties can be overcome with multiple anodes or a specially shaped anode that mimics the object geometry, however both of these solutions increase cost.

The current density strongly influences the deposition rate, plating adherence, and plating quality. This current density can vary over the surface of a part, as outside surfaces will tend to have a higher current density than inside surfaces. A higher current density results in a faster deposition rate. In order to solve these local uneven plating rates, the current is sometimes reversed. During this pulse-reverse plating some of the plating of the thicker parts dissolves. As a result of this the valleys are filled without over-plating the peaks. This method is commonly used on rough parts and/or when a bright finish is required.

There are two basic types of chromium plating: hard chromium plating and thin dense chromium plating. Hard chromium plating leaves a layer of chromium from 20  $\mu\text{m}$  to 125  $\mu\text{m}$  on the surface of the metal, while thin dense chromium plating generally has a chromium thickness from 5  $\mu\text{m}$  to 15  $\mu\text{m}$ . Chromium plating can be used over a wide temperature range from  $-57^\circ$  to  $427^\circ\text{C}$  and can withstand pressures up to 2068 bar. The temperature and pressure limits depend on the type of chrome plating, material substrate, and operating conditions. In most cases, thin dense chrome plating will provide better performance because of its greater fatigue strength (Ball seal eng, 2003).

Technochrome and DMI (Technochrome, 2010) uses this process with multiple electrodes and is specialised in chromeplating cylindrical metal tubes on a large scale, see for an example of the process Figure 5.1.

According to specification MIL-C-23422, Class 2 the dense thin layers must be crack and pinhole free. This means that certain chromium plating processes are able to produce thin dense chromium plating that is pinhole and crack free.



Figure 5.1 *Example of large scale chromium plating bath at Technochroom/DMI*

Electroplating of thin layers of pure palladium is done on a large scale by barrel and rack plating. Barrel plating is used in industrial palladium plating. It is the procedure for electroplating small parts in large quantities. The process entails tumbling the parts so it risks of damaging the shape. But in its entirety, it is a cost-effective procedure for palladium plating. Rack plating is the process of grouping individual parts together and then plating palladium as a group. Industrial metal plating using the rack method is done for electrical continuity. This process is considered more practical than having to individually plate each and every part.

Only palladium-nickel alloy deposition by electroplating was found in the available literature as an alloy application for the palladium. No other palladium alloys deposited on a large scale were found for the electroplating processes.

Electrodeposition of metals involves the movement of positive metallic ions towards the cathode to be reduced and finally be incorporated in the metallic growing film. This method can only be used on conducting substrates. The control of the film thickness depends several parameters like used electrolyte, temperature, pH and current density and time.

The electrodeposition of palladium has several variances. For example vacuum electrodeposition, where vacuum is applied to the cathode and pulsed electrodeposition where the electrical potential is pulsed in order to improve the uniformity of the deposition. Vacuum electrodeposition led to thinner and more selective films than electrodeposition according to Nam, 1999, Nam 2000. But these electrodeposition attempts for palladium membranes were done on lab scale. So far no large scale tubular shaped palladium membranes were electrodeposited. The application of a vacuum during the electrodeposition process promotes the penetration of the plating solution into the pores and pinholes and reduces the defects of the support membrane (Tian, 2005). The application of a vacuum can also be done during electroless plating.

The control over the deposition rate in the case of the electroplating method can easily be achieved by controlling the amount of the current passed through the electroplating cell. The co-deposition of two metals becomes difficult when the difference between the standard electrode potential of two metals is more than one volt. However, with the suitable combination of metal complexes, electrolyte and operating conditions, the deposition potential of the two metals can be brought closer and the co-deposition can be realised (Bhandari, 2010).

## 5.2 Fokker anodising

Fokker produces anodised aluminium surfaces by chromic acid production process on a large scale. Plates with dimensions up to 11 x 2.6 m and a thickness between 0.3 or 6 mm are anodised.

Fokker optimised this process for their plate dimensions. The bath chemistry contains phosphorous- and chromic-acid. The process window is not very critical for this bath chemistry. As a result defect free anodised layers with a uniform thickness of 3-5  $\mu\text{m}$  are formed during anodising on the AA2024 or AA7075 aluminium alloy surface.

Unfortunately, chromic acid is prohibited in the nearby future due to health/environmental issues. This means that the bath chemistry has to be changed. The plan is to use a phosphorous acid based bath chemistry for the anodising bath. This bath chemistry is more sensitive for pollution and the process window for a stable anodising process is very tight. Out of boundary process conditions will result in disastrous anodised layer results. This again emphasises the importance of the control of the bath chemistry related to the formation of a defect free layer with a uniform thickness.

## 5.3 Electroless plating

This process makes it possible to apply coating to interior surfaces of enclosures or housings. No conducting support is needed: even plastics can be covered by metals.

Selective platings can be deposited on surfaces. Thickness of 0.25  $\mu\text{m}$  to 0.50  $\mu\text{m}$  for Nickel is possible. Copper layers having a thickness of 2.0  $\mu\text{m}$  to 6.0  $\mu\text{m}$  are possible. Cybershield® is a company that uses electroless plating techniques for plated parts with the dimensions of 40 inches x 60 inches x 18 inches (46 cm x 101 cm x 152 cm).

Electroless nickel plating is generally used for housing/bore or parts with intricate shapes. This type of plating puts a uniform coating of approximately 3  $\mu\text{m}$  to 15  $\mu\text{m}$  radially. The hardness of electroless nickel plating is 48 to 52 Rockwell C for non-heat treated and 58 to 674 Rockwell C for heat-treated to 400°C for one hour. After plating, it just requires polishing the surface. Electroless nickel plating provides better corrosion resistance than chromium plating (Ball seal eng, 2003).

A very important issue is the control of the plating bath. Another issue is the requirement of high standards of quality control of the surface preparation and plating solution.

Various pre-plating steps are required to remove contaminations of the substrate surface. The electroless nickel plating process requires accurate control of the plating bath temperature, nickel content, pH level and filtration. A particular disadvantage of electroless nickel plating is that the bath can suddenly decompose in the presence of fine contaminant particles. Continuous filtration is required to prevent this.

Electroless nickel plating is done on an industrial scale. The number of pinholes for electrodeposited layers is often higher than the number of pinholes in electroless deposited layers. On an industrial scale electroless deposited Nickel layers are pinhole free at a thickness of 30  $\mu\text{m}$  while the electrodeposited Nickel layers are pinhole free at a thickness of 50  $\mu\text{m}$  (Schuring, 2006).

Improvements in bath chemistry, stirring etc. make it possible to manufacture thinner layers with lower pinhole densities.

A large scale palladium electroless deposition process is used in the semiconductor industries. Palladium surface finishes are used in printed circuit boards on copper surfaces. The ENEPIG process is an example of electroless deposition of various metal layers in which palladium is also deposited (Coombs, 2001). In this finish an electroless nickel layer of 3 to 6  $\mu\text{m}$  is deposited on the copper surface. This is then coated with an electroless palladium layer of a thickness of 0.1 to 0.5  $\mu\text{m}$  and finally topped with immersion gold at 0.02 to 0.1  $\mu\text{m}$ . The number of process steps for this sequence deposition process is shown in Table 5.1. The average layer growth rate for the electroless palladium plating process is estimated between 1  $\mu\text{m}/\text{h}$  and 1.5  $\mu\text{m}/\text{h}$  according to the information of Table 5.1.

Table 5.1 *Process steps of the electroless nickel/electroless Palladium/immersion*

Process step	Temp (°F)	Temp (°C)	Time (min)
Cleaner	95–140	35–60	4–6
Microetch	75–95	25–35	2–4
Catalyst	RT	RT	1–3
Electroless nickel	180–190	82–88	18–25
Catalyst	RT	RT	1–3
Electroless palladium	120–140	50–60	8–20
Immersion gold	180–190	82–88	6–12

Gold (ENEPIG) (Coombs, 2001).

The process steps of the ENEPIG process with explanation are presented below (Coombs, 2001):

- Cleaner: the purpose of this step is to clean the copper surface in preparation for processing. The cleaner removes oxides and most organic and inorganic residues and ensures that the copper surface will be uniformly micro-etched for catalyst uptake.
- Micro-etch: the purpose of this step is to micro-etch the copper and to expose a fresh copper surface that will catalyse uniformly. An appropriate etchant (for example, sodium persulfate, peroxide/sulfuric acid, etc.) may be used here.
- Catalyst: the purpose of this process step is to deposit an immersion coating of a catalyst on the copper surface. The catalyst lowers the activation energy and allows the nickel to deposit on the copper surface. Examples of catalysts are palladium and ruthenium.
- Electroless nickel: the purpose of this bath is to deposit the required thickness of electroless nickel on the catalyzed copper surface. The term electroless implies the presence of a reducing agent (sodium hypophosphite is the most common) to sustain the continuity of nickel deposition. The deposit is a nickel with 6 to 11 percent phosphorus. The thickness of the nickel should be adequate to create a diffusion barrier to copper migration and to serve as the solderable surface or as the contacting surface, depending on the intended use. The nickel bath has a relatively high deposition rate and its active chemical components must be replenished and maintained in balance on a continuous basis. Electroless nickel baths run at a high temperature and a long dwell time to achieve the required deposit thickness. One must ensure that material compatibility issues are understood and allowed for, such as choosing a compatible solder mask for the ENEPIG chemistry.
- Catalyst: the catalyst is an immersion palladium that is used to activate the nickel surface to facilitate the deposition of electroless palladium. It is similar to the catalyst used to activate the copper surface before electroless nickel deposition.
- Electroless palladium: the bath includes a reducing agent and thus is an electroless and not an immersion bath. Hypophosphite and bisulfite are reducing agents commonly used for this application. The hypophosphite gives a deposit with 1 to 2 percent phosphorous; the bisulfite gives a phosphorus-free deposit. The bath operates at 120 to 140°F (50 to 60°C). Dwell time varies from 8 to 20 min, depending on desired thickness.
- Immersion gold: in this step a thin, continuous layer of immersion gold is deposited. Immersion deposits are displacement reactions—gold displaces the palladium on the surface.

They do not require a reducing agent and are self-limiting as the palladium surface is coated with the immersion gold. This bath also runs at relatively high temperatures and dwell times.

Rinsing: rinsing is required after each chemical process step to remove all chemical residuals from the previous process step. This cleaning may be achieved using a single or dual rinse. Excessive dwell time in a rinse bath may cause oxidation or tarnishing of the product and is undesirable. Vendor specifications for temperature, dwell time, agitation, and turnover rate must be followed.

Disadvantages of this process are the length of the total process and the need for good process control (Coombs, 2001).

Another important disadvantage of this electroless plating process is the sources of waste that are generated during this plating sequence (Coombs, 2001), see Table 5.2.

Table 5.2 *Sources, waste streams and waste compositions from the ENEPIG palladium plating process (Coombs Jr, 2001)*

	Source	Waste stream	Composition
1	Cleaning and surface preparation	Spent acid/alkaline baths	Metals, acids, alkalis
2	Electroless plating and deposition	Spent electroless metal baths, Waste rinse water	Acids, palladium, complexed metals, chelating agents, formaldehyde
3	Pattern printing and masking	Spent stripper and developer solutions Waste rinse waters	Vinyl polymers, chlorinated solvents, organic solvents, alkalis
4	Electroplating	Spent plating bath Waste rinse waters	Metals, cyanide, sulphate
5	Etching	Spent etchant Waste rinse water	Ammonia, chromium, copper, iron, acids
6	Assembly	Aqueous and semi aqueous wastewaters	Lead, organics

Electroless plating processes are applied on a large scale in electronics and semi-conductor industries. (Clyde, 2001) compared the efficiency of electroless and galvanic plating for printed circuit boards. Printing wiring boards (= PWB) manufacturers, which are not familiar with electroless plating, often have the misconception that electroless plating takes 'too long'. On the contrary, electroless plating is faster than galvanic plating, and its volumetric efficiency is twice as much as galvanic plating.

Electroless plating baths operate at the layer growth speed of 2.0 to 5.0  $\mu\text{m}/\text{h}$ , 2.5  $\mu\text{m}/\text{h}$  being the medium speed. Because of its high throwing power<sup>†</sup>, a deposition thickness of 25  $\mu\text{m}$  on the panel surface also assures 25  $\mu\text{m}$  in the hole. That is, 10 h are needed to plate this thickness. The loading factor in electroless plating can be maintained at 4  $\text{dm}^2/\text{liter}$ . A 2500-gal (10,000-l) tank can plate about 400  $\text{m}^2$  of panels in one shot in 10 h. This is equivalent to twice the speed of galvanic plating from the same volume of plating solution. When small, high-aspect-ratio holes are involved, this figure becomes more favorable to electroless plating because the current density of galvanic plating must be reduced to 10 to 12  $\text{A}/\text{ft}^2$ , which requires more than 2 h of plating for 25  $\mu\text{m}$  in the hole.

<sup>†</sup> Throwing power = the ability of an electroplating solution to deposit metal uniformly on an irregularly shaped surface.

On non conducting substrates electroless plating is an advantage. Limitations which characterise for example electroless gold plating processes are:

- plating rates are low,
- controlling of the plating conditions is critical,
- substrates must be thoroughly cleaned,
- plating baths tend to have relatively short lives,
- the thickness distribution of deposits is sensitive to stirring conditions.

The volume to area ratio's of the bath in electroless plating is also very critical.

Electroless plating is one of the more popular deposition techniques that were found in the available literature for depositing thin Pd alloy films on various tubular supports. Unfortunately only binary Pd-Cu and Pd-Au systems are studied intensively next to the electroless plated pure Pd thin layer membrane system.

Often the bilayer sequential plating method was used. The bilayer method consisted of depositing a thick layer of Pd (4.5  $\mu\text{m}$ -10  $\mu\text{m}$ ) already selective to  $\text{H}_2$  followed by the Ag layer on the top. The bi-layer was annealed at high temperature to form the Pd-Ag alloy. (Bhandari, 2010) reviewed the literature in which the results of several bi-layer attempt for Pd-Ag membrane systems were presented. It can be concluded that the relatively thick layers that are formed by the bi-layer method requires very long annealing times at high temperatures while there is still a distribution of Pd and Ag across the cross section of the bi-layer. This makes the electroless bi-layer membrane production method less suitable for an industrial large scale manufacture route, and unfeasible for homogeneous membrane production.

The annealing temperature and time can be reduced by using the multi-layer sequential deposition approach. The multi-layer sequential deposition approach allows deposition of very thin layers (1-2  $\mu\text{m}$ ) of Pd and Ag which then could be annealed using the short time and lower temperature than that required for the bi-layer approach.

An alternative way to the sequential deposition method is the co-deposition method for the preparation of the Pd-Ag membranes. The co-deposition method simplifies the plating steps involved in the Pd-Ag deposition and if the co-deposits have small size Pd and Ag particles, the annealing of the membrane also becomes relatively easier. Pd-Ag co-deposition only occurred for 0-20 wt% Ag. For higher Ag concentrations only Ag deposition occurred.

It is clear from the literature done by (Bhandari, 2010) that various electroless deposition methods can result in the formation of a Pd-Ag membrane surface. Although among others (Bhandari, 2010) claims that electroless deposition methods are relatively simple and has the potential for scaling-up, no examples of large scale tubular palladium alloy membranes were found in the available literature that were made by the electroless deposition method. This was only found for pure Pd membranes made by an electroless deposition process.

Although the electroless deposition methods for the manufacture of palladium alloy membranes looks very promising on a lab-scale, it is questionable whether this method will be a successful route for the production of palladium alloy membranes of binary or multi component palladium alloy membranes on a large scale. Difficulties like control of the overall film thickness of the palladium alloy membrane surface, development of suitable and stable chemical baths are issues that have to be solved first.

## 6. Thermal spray techniques

Powders for thermal spray techniques can be produced by techniques like spray pyrolysis and gas atomisation. Pd-Ag submicron sized particles were produced by ultrasonic spray pyrolysis. No data was found in the available literature on the production of thermal spray particles in the Pd ternary alloy range of interest.

Another proven technology is gas atomisation. Several companies like TLS technik Spezialpulver and Atomising systems limited. Gas atomisation is a technique where a rotating electrode of the preferred alloy content is melted by an induction coil. A thin film of liquid metal flows down a cone of the electrode. The molten metal is led through a gas nozzle system where the metal is atomised. There is no change of chemical composition of raw material during atomisation. Gas atomisation produced spherical powders. The limitation of gas atomisation is the particle size. The particle size is around 10  $\mu\text{m}$ . This is very large in comparison with the required of Pd alloy membrane thickness of  $< 5 \mu\text{m}$ .

Another problem is the amount of permeable pores in relation to the thickness of the thermal sprayed layer. Thermal spraying techniques and layer thickness are related. Thermal sprayed layers suffer from the fact that the deposited layers are porous. High velocity oxygen fuel (=HVOF) thermal sprayed palladium layers were deposited on a support (Hollein, 2001). Relatively large layer thicknesses are deposited by thermal spraying in order to avoid permeable pore formation. This increased layer thickness will result in a decreasing permeability and increasing costs. (Hollein 2001) compared electroless plating and HVOF (high velocity oxygen fuel) thermal spraying of palladium onto porous stainless steel and alumina tubes. Thicknesses of the Pd-layers  $\geq 3$  (electroless plating) and  $\geq 50 \mu\text{m}$  (HVOF) were necessary to get defect-free films (Hollein, 2001). High-temperature permeation tests (350–650°C) were carried out to determine the permeation properties as well as the thermal and mechanical stability of the prepared membranes.



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## 7. Laser assisted deposition

### 7.1.1 Laser Assisted Deposition

Several methods exist where lasers apply a material onto a surface. Many of these methods are in an academic phase, few are (semi-) industrial and often these methods are variations of others.

- **Laser Metal Deposition:** a well-known technology, also known as Laser Cladding. A metal powder is applied onto a surface and (at the surface) heated by a laser. The power melts and solidifies onto the surface. This technique is used for hardening of tools, repair of machine parts, etc. The choice of metal powder (or its alloy) determines the quality. Generally, the result is a sintered layer with pores (and this is for ECN's application not acceptable). The achievable thicknesses are in the order of tens of micrometers or more. This method is not suitable, because it can not fulfill the requirements on thickness and absence of pinholes. Even if these drawbacks can be counteracted, the metallurgical impact (making an alloy out of pulverised metals) might be problematic.

An overview of other laser assisted deposition techniques is listed by (Kordas, 2001). The best known:

- **Pulsed Laser Deposition (PLD)** is a Physical Vapour Deposition technique. A target with material to be deposited is heated with a laser pulse. Material ablates and a plasma plume appears. The evaporation/ablation ejects the material/plasma towards the deposition surface. An Ultra High Vacuum is necessary, although for some applications the use of additional gasses is beneficial (to modify the deposition result). This is a technique which is applicable for small parts and not for the large areas which are required for the membrane application.
- **Laser-assisted Chemical Vapour-Phase Deposition (LCVD).**
- **Laser-induced Forward Transfer (LIFT).**

According to (Kordas, 2001) these known technologies can be used on insulators but require vacuum, gas systems and sometimes (LCVD) dangerous compounds.

Currently, there seems not to be an industrial process to bring the base material/alloy onto the ceramic using a laser.

### 7.1.2 Pulsed laser deposition

On the website of the Opto-electronics Research Centre of the University of Southampton the principle of Pulsed Laser Deposition [PLD] is briefly introduced [see website: <http://www.orc.soton.ac.uk/pld.html>]: "PLD is a versatile technique for growing thin films and can be applied to a very wide range of materials. A pulsed laser (usually ultra-violet (UV) wavelength) is used to ablate a target, and a plasma plume is formed by the ejected material; the plasma plume then expands away from the target surface and interacts with the chamber atmosphere until it reaches the substrate, where it is deposited as a thin film. The substrate can be heated to assist with nucleation and allow crystal growth, and a background gas can be used to help control the film composition. The PLD process covers many different areas of physics and chemistry, and an increasing understanding of what drives the mechanisms behind successful depositions is critical for the continuous improvement of future films and devices. Several deposition parameters must be carefully optimised before high quality films can be produced. A major advantage of the technique is the occurrence of stoichiometric transfer. This

allows complex multi-component materials to be grown and has the added benefit that targets can be adapted easily from small pieces of bulk material".

The group working on various aspects and applications is headed by Prof. Robert Eason, who also was the editor of one of the handbooks on PLD (Eason, 2007). A graphical representation of the process is given in Figure 7.1.

For PLD a (ultra high) vacuum is necessary, although depending on application gasses may be added in the processing chamber. Gas can be used as reactant during travelling of the target material to the target surface (e.g. oxidation) or the gas is used to decelerate the material in the plasma to prevent too high speed at the target surface.

Multiple materials can be deposited by using multiple targets (targets are on a carousel and subsequently the targets are moved under the laser position). Another way is to start with a target containing the different materials. The problem in the latter case is that the different compounds in the target will react differently on the laser pulse (different evaporation temperatures, different vapour pressures). By adjusting the laser settings and/or changing the relative occurrence of the compounds, the deposited film might contain the correct material contents.

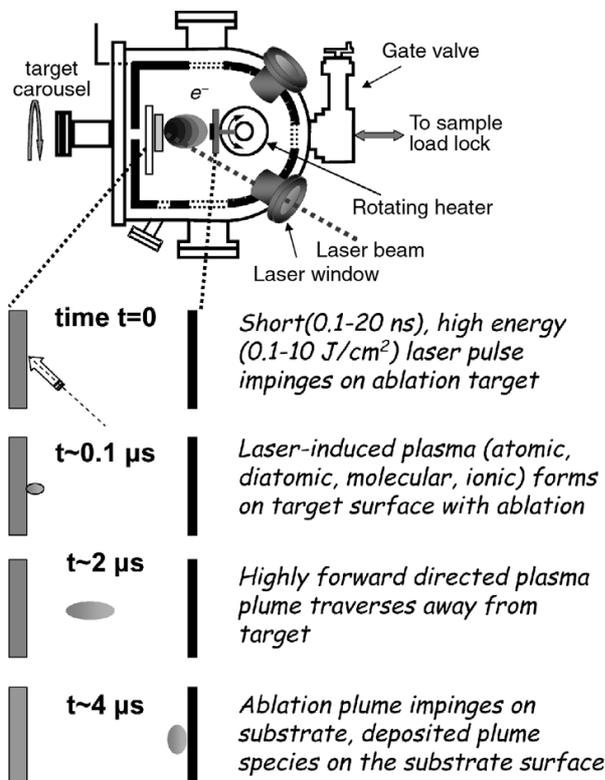


Figure 7.1 Principle of pulsed laser deposition (PLD)

From a processing point of view: usually one laser is enough. All metals considered here (see chapter 2) have relatively high reflection coefficients (>75%); the longer the wavelength, the higher the reflection coefficient. Therefore short wavelengths (UV) are more beneficial. Furthermore short pulses (short nanosecond) are used. (Currently, picosecond and femtosecond UV are also used merely for academic purposes). Because of short pulse length and wavelength mostly excimer lasers are used. These lasers are bulky, expensive to operate and often must be used with utmost care (because Cl or F is used in them).

Laser-deposited films are often much more homogeneous than sputtered or evaporated films according to (Eason, 2007). For instance, in the case of PLD, decomposition of Fe-Nb is not present at all. In contrast to sputtered films, laser-deposited samples are either completely amorphous or supersaturated solid solutions. For other systems like Co-Cr, the homogeneity of the deposited alloys was confirmed on an atomic scale by field-ion microscopy combined with an atomic probe (FIM/AP), while sputtered films decompose during deposition. Nevertheless, in demixing systems like Co-Cu, Fe-Ag, Ni-Ag, or Fe-In, the decomposition could not be prevented at medium concentrations as confirmed by FIM/AP, transmission electron microscopy (TEM), and X-ray diffraction. Atomic mixing processes induced by deposition and implantation of energetic particles seem to be responsible for the better film homogeneity.

At the moment no such comparison was found for palladium alloys deposited by pulsed layer deposition in the available literature.

One of the main application areas for PLD is the manufacturing of High Temperature Superconductors (HTS). Furthermore, the technology is used in the semiconductor-, opto-electronic- and electronics industries. A short survey on commercially available systems show that up to 8" (200 mm) diameter wafers can be processed. For the HTS application there are also roll-to-roll systems available, to make HTS tape.

In all these cases the sizes of the products ranges from cm's to maximal decimeter scales and are much smaller than required for the Pd-membranes application.

Given the porosity, size and fact that a cylindrical geometry must be covered, this application is far away from the current application fields. Because of these discrepancies there has been a very brief enquiry about the feasibility of the ECN application at one of the suppliers of PLD systems (Greer, 2010). (Other suppliers are e.g. <http://www.neocera.com> and <http://www.nbmdesign.com/pld-systems.html>)

According to J. Greer of PVD Products Inc. (<http://pvdproducts.com>), Wilmington, USA it would be possible to build a system for this geometry. However, J. Greer estimated that sputtering is a much more reliable and cheaper solution considering requirements and geometry.

Currently, there seems not to be a laser deposition based industrial process to bring the base material/alloy onto the ceramic.



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## 8. Vacuum deposition techniques

Vacuum deposition is used in a wide variety of industries, including semiconductors, machine tools, razor blade manufacture and packaging (Cheng, 2003). Typically, the required material is vaporised in vacuum and allowed to condense on the items to be coated. In another method, called "sputtering", a directed flux of ions (mostly  $\text{Ar}^+$ ) eject material, without the need for heating, by atomic collisions occurring at or near the surface. This is the preferred method for deposition of alloys or mixtures of controllable composition. At a manufacturing level, vacuum-based processes can be cost-effective.

A web coater, or roll coater, is designed to treat material in a thin film form, and it is the most efficient means for treating large areas. A roll of substrate that is wound through a coating machine, is called a web. The terms roll coater and web coater are often used for the same principle of the coating process.

In the case of web coaters, flexible polymer and metallic substrates have been coated with a variety of metal and ceramic materials for use in capacitors, magnetic media, thin film batteries and food packaging. In a vacuum web coating system, materials are typically condensed out of a physical vapour by either thermal evaporation or magnetron sputtering processes onto a continuous moving web such as plastic film. The plastic film can have dimensions like a broadness of meters and a theoretically infinite length.

The most commonly used techniques for producing thin metal membranes next to electroplating on porous supports are chemical vapour deposition and physical vapour deposition.

### 8.1 Chemical vapour deposition

Chemical Vapour Deposition (CVD) is the reduction or decomposition of a volatile compound of the coating material upon a heated surface. CVD allows depositing coatings of most refractory metals while other techniques are unsuccessful. CVD leads to pure and thin layers on small substrates. However the procedures are tedious and nearly impossible for industrial purposes. Metal-Organic Chemical Vapour Deposition (MOCVD) differs from CVD in that only high purity organo-metallic compounds are used. Another major disadvantage of CVD is the unavailability of inexpensive precursors with desired volatility and chemical properties.

### 8.2 Atomic layer deposition

Using ALD, film thickness depends only on the number of reaction cycles, which makes the thickness control accurate and simple: about one layer per cycle. Unlike CVD, there is less need of reactant flux homogeneity, which gives large area (large batch and easy scale-up) capability, excellent conformity and reproducibility. Also, the growth of different multilayer structures is straight forward. These advantages make the ALD method attractive for microelectronics for manufacturing of future generation integrated circuits. Other advantages of ALD are the wide range of film materials available, high density and low impurity level. Also, lower deposition temperature can be used in order not to affect sensitive substrates (Aaltonen, 2005).

ALD has several limitations. The major limitation of ALD is its slowness; usually only a fraction of a monolayer is deposited in one cycle. Fortunately, the films needed for future-generation integrated circuits (=IC's) are very thin and thus the slowness of ALD is not such an important issue. Although the selection of film materials grown by ALD is wide, many technologically important materials (Si, Ge, Si<sub>3</sub>N<sub>4</sub>, several multi-component oxides, certain metals) cannot currently be deposited by ALD in a cost-effective way [ALD 2010]. ALD is a chemical technique and thus there is always a risk of residues being left from the precursors. The impurity content of the films depends on the completeness of the reactions. In typical oxide processes where metal halides of alkyl compounds are used together with water as precursors, impurities found in the films are at the 0.1-2 atom % level (Aaltonen, 2005).

Growth rates for Pd layers are of the order of  $0.2 - 1 \cdot 10^{-10}$  m/cycle (Elam, 2006). A layer of  $400 \cdot 10^{-10}$  m (= 40 nm) requires 3000 cycles. The total cycle time is approximately between 4 s - 8 s.

Although the accurate thickness control is a benefit of the ALD process, the growth rate is very low. This makes this process not appropriate for large scale manufacture of palladium alloy membranes.

Fast ALD is an innovation of the classic ALD process (Vincken, 2010). Layer growth rates of 1.2 nm/s can be obtained which is faster than the layer growth rate of 0.1 nm/s for the classic ALD systems (Gortzen, 2010).

Based on a private communication with Roger Gortzen business developer at TNO it became clear that the Fast ALD system is still under development. Samples with a diameter of 100 mm were coated with a SiO<sub>2</sub> layer.

### 8.3 Sputtering

Sputtering deposition is considered as one of the physical vapour deposition methods. The process can be conducted under ambient substrate conditions or elevated substrate temperatures. Compared with other conventional methods, sputtering deposition exhibits a good control of film thickness and composition. Meanwhile, it has the advantages of faster deposition rate and low operational temperature. However, the thin films coated by sputtering technique are very sensitive to the surface conditions (morphology, purity, material type) of the substrate on which they are supported. This might lead to the failure in obtaining gas tightness on deposited film and even peeling-off of the film from the substrate.

During sputtering, energised plasma ions strike a 'target', composed of the desired coating material (pure Pd or a Pd alloy), and cause atoms from that target to be ejected with enough energy to travel to, and bond with, the porous substrate. This method can be used for the highest melting point materials while evaporation of these materials is problematic or impossible.

There are several types of sputter deposition techniques. Magnetron sputtering is the most common sputtering technique. The sputtering target is acting as a magnetron that utilise a strong magnetic and electric field in order to trap electrons and ions close to the target surface. The amount of collisions is intensified and results in an intense plasma and higher deposition rate. Co-sputtering is a method where several magnetron targets are used. The composition is controlled by changing the power to the individual targets. Substrate rotation is required in order to get compositional uniformity.

AC or RF sputtering is sputtering where a high-frequency generator is used generating electromagnetic power in the MHz region (typical: 13.56 MHz) between the target and the ground. RF sputtering is for example used for depositing from insulating layers and reduces charge-up effects on the substrates kating layers

On average sputter deposition rates can range from 1  $\mu\text{m/h}$  to 10.0  $\mu\text{m/h}$  (Chachetto, 2004). The most commonly applied materials are chromium, titanium, aluminum, copper, molybdenum, tungsten, gold, and silver.

Sputtering allows for the depositions of films having the same composition as the target source. This is a primary reason for the wide spread use of sputtering to deposit metal alloy films (Ohring, 2002). However each alloy component evaporates with a different vapour pressure and sputters with a different yield. However, contrary to evaporation film, stoichiometry can still be maintained during sputtering.

It is possible to fine tune the deposition rates by using multiple targets or using targets with the alloy composition that has to be deposited (Ohring, 2002).

## 8.4 Ion beam and e-beam evaporation

A similar technique, electron beam (e-beam) evaporation can be used for Pd and Pd-alloy deposition. In e-beam evaporation the porous substrate is placed in a high vacuum chamber at a desired temperature with a crucible containing the material to be deposited. An electron beam is aimed at the material in the crucible causing it to evaporate and condense on all exposed surfaces in the vacuum chamber and substrate. Several crucibles, with different compounds (or metals), are available in the same chamber and switching crucibles leads to the evaporation and condensation of different compounds

Ion-Beam (i-beam) evaporation is essentially the same as e-beam but using argon ions instead of electrons. Magnetron sputtering, e-beam evaporation and ion beam evaporation, which are called physical vapour deposition (PVD), are generally applied when depositing alloys. The main drawback of these techniques is that the vacuum chambers have a confined space and coating of large supports for large scale high purity  $\text{H}_2$  membrane production is a problem. So up scaling will be very unlikely.

## 8.5 Industrial large scale vacuum deposition techniques

The deposition of thin metal or thin material films on a very large scale is used in the packaging, automotive, solar and semi-conductor industries. Several examples of commercial available systems will be given in this paragraph. Roll-to-roll systems or web coater systems are examples of these large scale vacuum deposition techniques.

Vacuum coating is used in many applications. Several of these applications are summarised below.

### 8.5.1 Solar industry

In the solar industry, several thin film deposition techniques like: PECVD, MOCVD, (co)-sputtering, (co)-evaporation, paste, inkjet, electroplating, nanoparticle/Sol-Gel etc. are used. Also here is a drive towards high production rates and reducing costs. One example of a large scale sputtering device that is designed by Leybold is shown in Figure 8.1.

## Concept for CIGS solar cells on metal strips

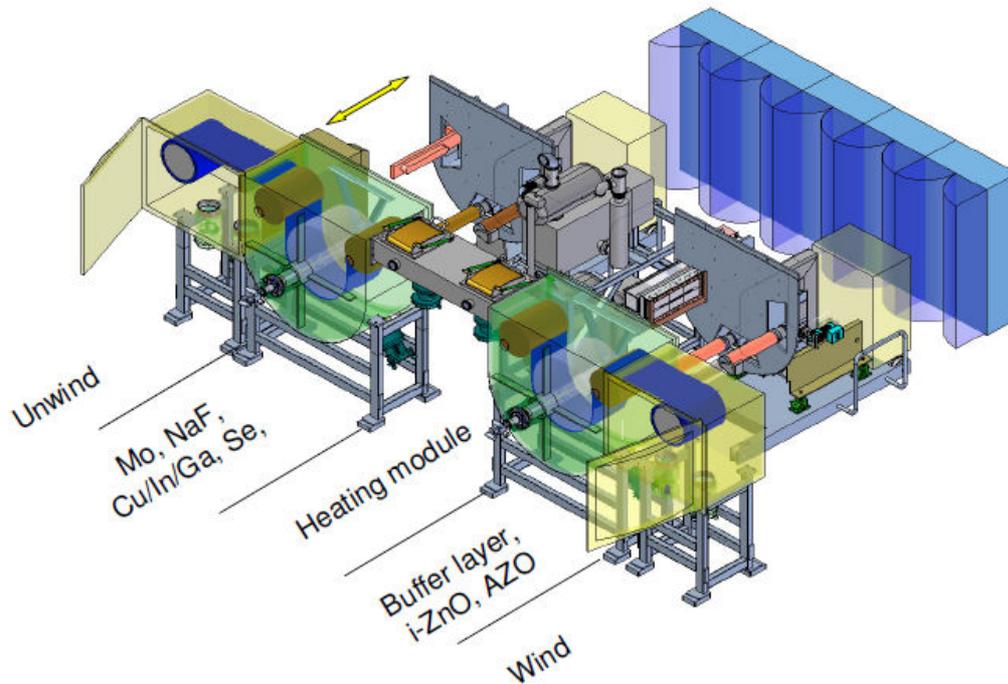


Figure 8.1 *Sputter system for large scale manufacture of CIGS solar cells on metal strips*  
(Liehr, 2007)

### 8.5.2 Large scale metallisation roll-to-roll

The added value in packaging materials is combination of film products in order to have special properties. Metal films on the polymer based foils/films are often applied in the food industry or for the production of insulation foils. An aluminium layer with a thickness between 20  $\mu\text{m}$ -25  $\mu\text{m}$  is impermeable for water and oxygen. Deposition of metal film on large area polymer materials is on an industrial scale done by vacuum web coating. This process is used in industries like electronics, consumable/food industry

Applied Materials delivers systems that are used for large scale metallisation. Applied Materials TOPMET roll-to-roll coating system provides the latest production solutions for the packaging industry. Utilising a thermal evaporation process, thin layers of aluminium are metallised onto flexible substrates, like plastic or pre-coated paper, for production of protective packaging or decorative materials. TOPMET offers state-of-the-art engineering, equipped with advanced high rate evaporation sources, closed-loop automatic layer control, self-diagnostic out of range monitoring, and high performance pumping systems. As the industry leader for innovative production solutions, this system is available in various coating widths ranging from 650 mm to the world's largest system at 4500 mm in width, with an astonishing speed of up to 17 meters per second. Efficient use of raw materials and power, fully automated process control and ease of operation ensure lowest overall operation costs, consistent coating uniformity along with the in-line plasma pre-treatment to improve bonding strengths and gas permeability. An aluminium layer of 25  $\mu\text{m}$  is impermeable for water and oxygen. This means that the deposition rate or better the layer growth rates are extremely high.

### 8.5.3 Flexible electronics (Ludwig, 2005)

Going flexible seems to be a major trend for a variety of electronic applications such as displays, printed circuit boards, solar cells, and solid-state lighting. Driving forces, which may often include the function of 'flexibility', are the potential to build units with less thickness and with less weight or the ability for very-large-area applications. Last but not least, there is the need for a remarkable reduction of production costs, which can be fulfilled by changing the production process from sheet processing to roll to roll. The first vacuum web coater was built 70 years ago, and vacuum web coating is currently used for a wide variety of applications. In the packaging industry, aluminium coating is primarily used for barrier improvement of plastic substrates. Such coatings are deposited with an evaporation process in machines of up to 4-m coating widths on rolls up to 60,000 m length and at coating speeds of more than 16 m/s. For capacitor production, thin webs with thicknesses down to the sub micrometer range are vacuum-coated with aluminium, silver, or zinc layers, and uncoated stripes or patterns are also needed. Vacuum-coated web-shaped substrates can also be used for antireflective, antistatic function in the front of monitors, as window films for cars and architectural applications or as front electrodes for touch panels as a few examples.

Different coating tools such as evaporation, sputtering, plasma-enhanced chemical-vapour deposition (PECVD), as well as pre-treatment tools and inline layer measurement systems are available. Many of the currently available tools and processes existing in the web coating industry may become useful for upcoming electronic applications, but special demands for these new applications, such as exact area tracking, zero defects, roll-to-roll masking, and reduced substrate temperature during coating, require further development of machine design and process technology.

### 8.5.4 Packaging (Ludwig, 2005)

Barrier coatings are used on flexible polymer films and paper for food packaging to reduce the water vapour transmission rate (WVTR) and the oxygen transmission rate (OTR) through the paper or polymer film. The most common barrier coating material is aluminium, which is deposited on rolls of polymer film (web), then supplied to 'converters' who fabricate the packaging. In some cases the metal coatings are deposited on a surface and then 'transferred' to the packaging film. Transparent barrier coatings are desirable in many instances. Layers of  $\text{SiO}_2$ , by reactive evaporation and PECVD and composite coatings of  $\text{SiO}_2$ :30%  $\text{Al}_2\text{O}_3$  by e-beam co-evaporation are used to form transparent barrier layers. The composite coating material is more dense and flexible than the  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  deposited material alone. Aluminium films are used on polymer helium-filled balloons to reduce the loss of helium.

### 8.5.5 Freestanding Films/Structures (Ludwig, 2005)

Freestanding structures can be made by depositing a coating on a surface (mandrel), then separating the coating from the mandrel surface or dissolving the mandrel. The technique is useful for fabricating very thin structures, complex surfaces, or foils or sheets of materials that are hard to deform by rolling. Examples are beryllium windows used for X-ray transmission, boron thin-wall cones for high-frequency audio speakers, and Ti-V-Al metal alloy foils. A relatively new application is the production of micro-electromechanical systems (MEMS) devices where very small structures are fabricated using deposition and etching processes.

### 8.5.6 Automotive

Leybold optics has a 3D sputter coating system for metallising large and complex three-dimensional parts, Figure 8.2. This system is available in many different versions. For example the Pylonmet sputtering system can sputter substrates with a diameter of 750 mm and a length of 1270 mm. At this moment this 3D coater system is used for sputtering metal coatings on reflectors for automotive applications. According to Leybold it is not impossible to sputter coat a palladium alloy film on a porous substrate with this polymet system. Larger size tubular support requires a change in the design of the vacuum chamber.



Figure 8.2 *Photo of the polymet 3D coater from Leybold showing the metallised reflectors for automotive applications*

## 8.6 HEF group

Based on a private communication with Hervé Delorme from HEF it became clear that HEF has a 2.1 meter long vacuum chamber in their sputtering system. HEF sputtered Pd-Ag film on disc shaped ceramic surfaces with a diameter of 10 cm. This work was done for IFP. No data was available on the layer thickness and pinhole formation on these sputtered ceramic samples.

## 8.7 Semi-industrial scale: palladium alloy film manufacture

### 8.7.1 SINTEF

SINTEF developed a two step route for the manufacture of thin film Pd-Ag. In the first step a thin Pd-Ag film was sputtered on a polished oxidised silicon wafer. In a second step these films were released and wound around a porous support, see Figure 8.3.

Results of the hydrogen flux and  $H_2/N_2$  separation factor as a function of the feed side pressure at a temperature of  $400^\circ\text{C}$  obtained in a 50%  $H_2$  + 50%  $N_2$  mixture are shown in Figure 8.4. The Pd-23wt%Ag membrane film has a thickness of  $2\ \mu\text{m}$ .

The long-term stability of Pd-23%Ag/stainless steel composite membranes has been examined in  $H_2/N_2$  mixtures as a function of both temperature and feed pressure (Peters, 2008; Peters, 2009). During continuous operation, the membrane shows a good stability at  $400^\circ\text{C}$  while the  $N_2$  leakage increases very slowly at a temperature of  $450^\circ\text{C}$  ( $P_{\text{feed}} = 10\ \text{bar}$ ). After 100 days of operation ( $P_{\text{feed}} = 5\text{--}20\ \text{bar}$ ,  $T = 350\text{--}450^\circ\text{C}$ ), the  $N_2$  permeance equals  $7.0 \times 10^{-9}\ \text{mol m}^{-2}\ \text{s}^{-1}\ \text{Pa}^{-1}$ , which indicates that the  $H_2/N_2$  permselectivity still lies around 500, based on a  $H_2$  permeance equal to  $3.0 \times 10^{-6}\ \text{mol m}^{-2}\ \text{s}^{-1}\ \text{Pa}^{-1}$ . Despite the generation of small pinholes, a membrane life-time of several (2–3) years ( $T \leq 425^\circ\text{C}$ ) is estimated for the experimental conditions employed based on long-term stability tests over 100 days.

Post-process characterisation shows a considerable grain growth and micro-strain relaxation in the Pd-23%Ag membrane after the prolonged permeation experiment. Changes in surface area are relatively small. In addition, segregation of Ag to the membrane surfaces is observed. The formation of pinholes is identified as the main source for the increased  $N_2$  leakage during testing at higher temperature.

SINTEF found that formation of pinholes started at  $400^\circ\text{C}$ – $450^\circ\text{C}$  during long term stability tests. They solved this issue by the application of some intermetal diffusion barrier on the porous SS PSS® support (Peters, 2008).

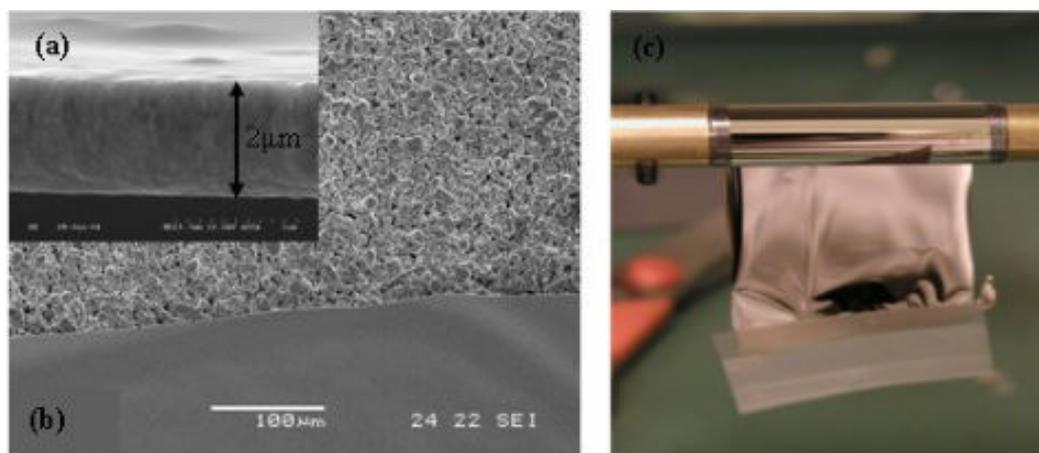


Figure 8.3 (a) A cross section of the unsupported Pd-23wt%Ag film. (b) Top view of the PSS® support showing the interface with the Pd-Ag film. (c) Example of a tubular supported membrane (Peters, 2008)

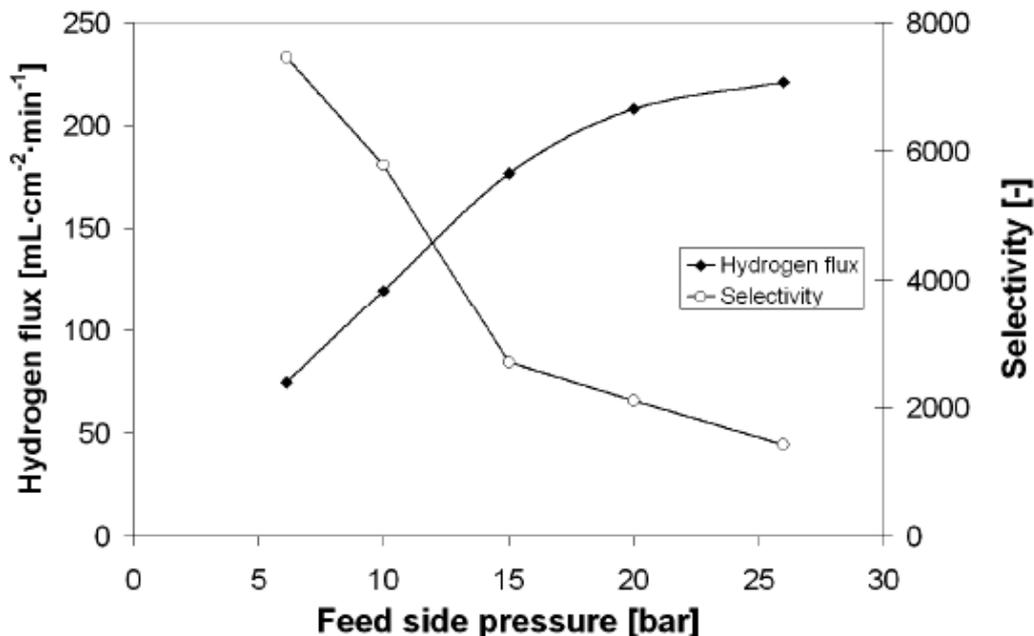


Figure 8.4 Hydrogen flux and  $H_2/N_2$  separation factor as a function of the feed side pressure at a temperature of  $400^\circ\text{C}$  obtained in a 50%  $H_2$  + 50%  $N_2$  mixture (Peters, 2008)

### 8.7.2 SwRI

SwRI first developed a route in which they used e-beam evaporation and magnetron sputtering of a thin Pd-Cu film on a polymer backing material (PS, PVA, Kapton, and PET) in a continuous manner, see Figure 8.5.

Although procedures were developed and routinely employed to deposit and release Pd-Cu films, 2-5  $\mu\text{m}$ -thick and  $>484\text{ cm}^2$  in area from PS and PVA polymer backing materials through-thickness defects (pinholes) for film thicknesses less than 6  $\mu\text{m}$  were significant (Coulter, 2008).

Although argon plasma treatment (with 5%  $\text{O}_2$ ) was shown to decrease water contact angles (increase film wettability) on all plastics tested (PS, PVA, Kapton, and PET), defects in films less than 5  $\mu\text{m}$  remained. Therefore, irrespective of the surface treatment options tested (plasma or seed layer), defect free Pd-Cu films on flexible polymer substrates over large areas at thicknesses  $<5\text{ }\mu\text{m}$  could not be produced. It is important to note however that defect-free films were produced at thicknesses  $>6\text{ }\mu\text{m}$ .

For all alloy films produced to this point, SwRI was unable to produce pinhole-free films on plastic although they were able to produce free-standing Pd-Cu films at less than 0.5 microns thick with minimal intrinsic stress (Coulter, 2008).

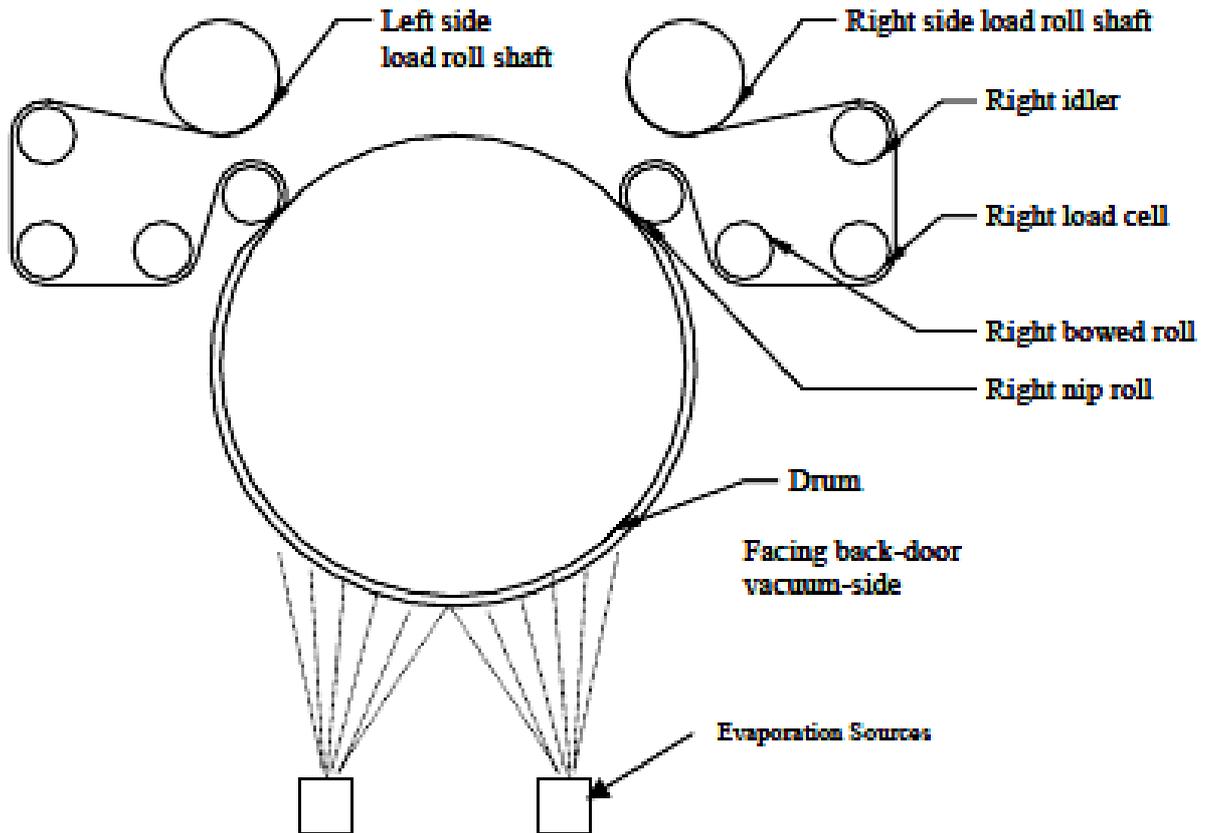


Figure 8.5 Schematic of web roll coater with evaporation sources as used by SwRI (Coulter, 2008)

As an alternative to address the issue of defects in the Pd-Cu alloy membrane on flexible substrates, films were deposited onto smooth, thermally oxidised silicon wafers (Coulter, 2008). The reasoning was that particulate and other contaminants can be more readily controlled (i.e., minimised) on a silicon surface in comparison to plastic, and is considerably smoother than plastic. In preliminary experiments using magnetron sputtering, a relatively pinhole-free ( $< 740$  counted pinholes/m<sup>2</sup>) coating was produced that easily released from the silicon substrate (poor adherence). In general, the key factors that affect formation of a thin, dense, defect-free, Pd-Cu alloy film are surface energy, roughness, and oxygen/moisture content of the backing material.

In principle the SINTEF method is comparable with the SwRI method.

New procedures were developed and implemented to improve reliability and repeatability of release characteristics from the temporary substrate (i.e., silicon wafer) and to minimise through thickness defects in a 12" diameter film, 3 microns in thickness. With the new procedures, stress free films, with zero or minimal defects (less than five) across a 12" diameter area were consistently produced, see Figure 8.6.

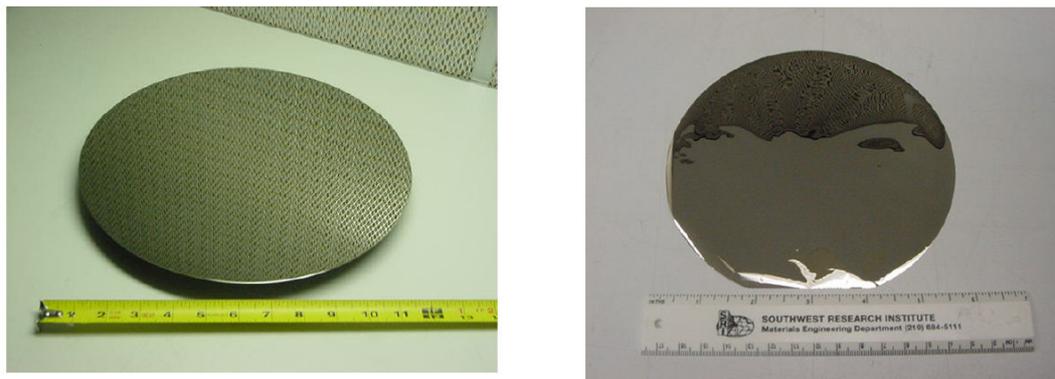
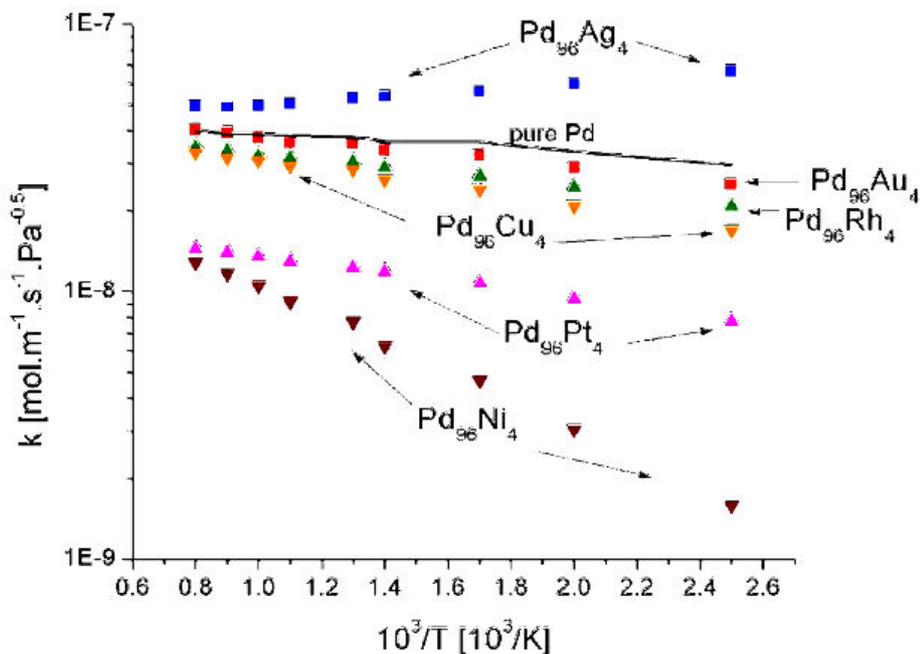


Figure 8.6 (left) Pd-Cu membrane grown on a polished and oxidised 12 inch silicon wafer. (right) As-deposited and released 3 µm thick Pd-Cu film (Coulter, 2008)

As the membrane material built up on the silicon support, the sample was rotated and translated across the Pd-Cu sputter target. The average thickness of this membrane was 5.3 microns with a thickness variation of approximately 20%. By using a larger sputter target or a different rotation/translation pattern, the thickness variation could be reduced to less than 5%.

SwRI predicted H<sub>2</sub> permeabilities based on DFT models, see Figure 8.7. In an effort to experimentally validate some of these predictions, sputtering with multiple targets such as Ru, Rh, and Ta was done. Magnetron sputtering is uniquely suited for the rapid preparation and screening of new ternary alloys because the composition can be quickly changed simply by tiling different areas of material on the target.

As an example H<sub>2</sub> permeability test results of various palladium alloys are shown in Figure 8.8 and Figure 8.9. For experimental details is referred to (Coulter, 2009)



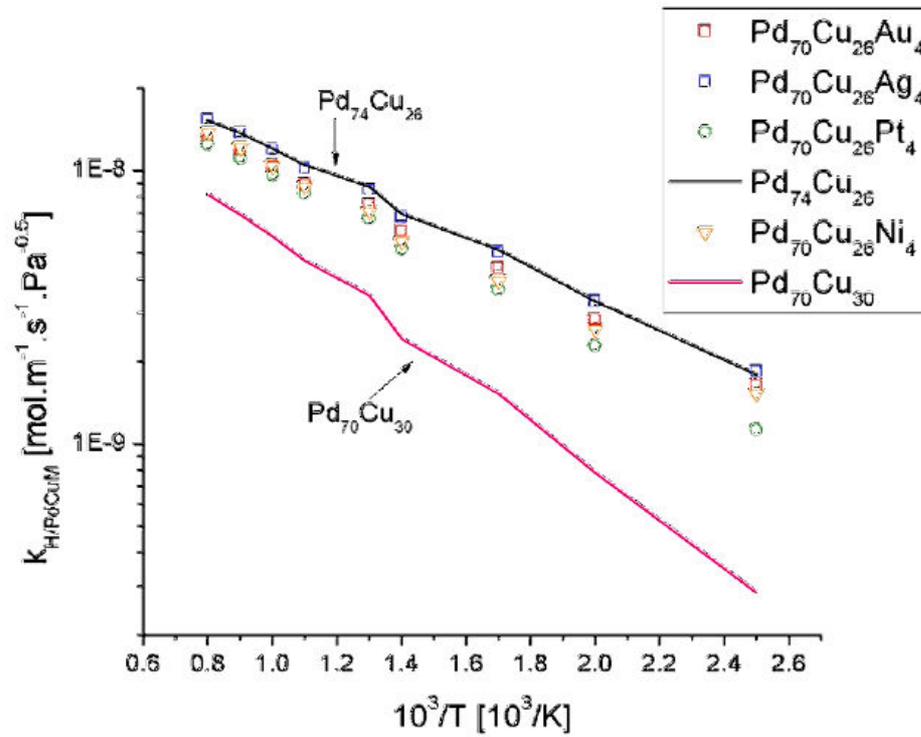
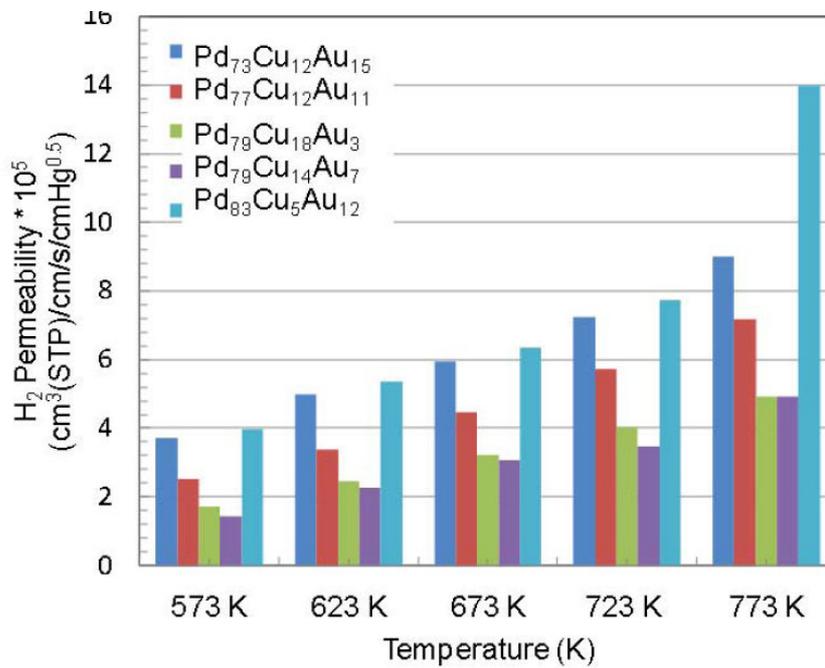


Figure 8.7 Predicted permeabilities of binary and ternary alloys, based on DFT models (Coulter, 2009)



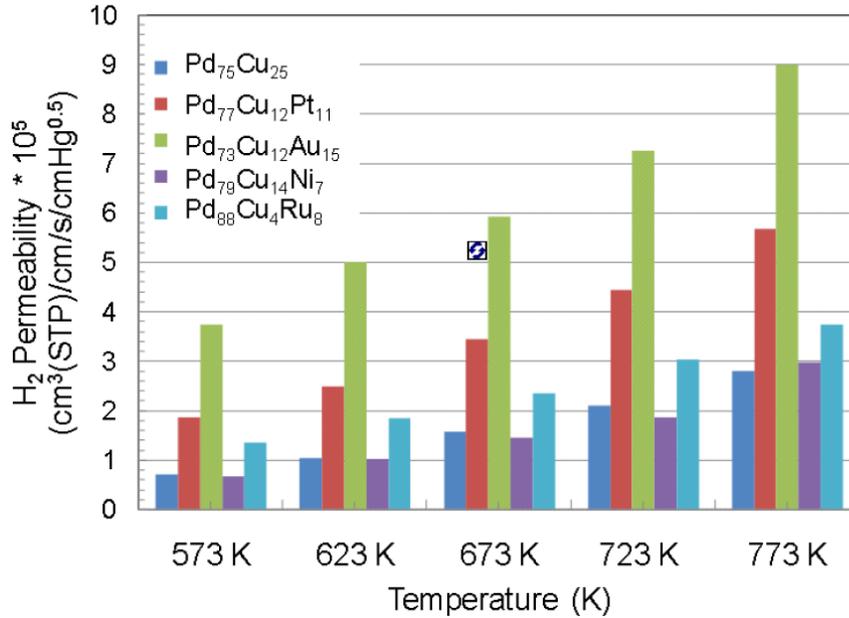


Figure 8.8 Hydrogen permeability results as a function of temperature for (top) different ternary PdCuAu alloys and (below) binary PdCu and ternary alloys PdCuX with X=Pt, Ru, Ni and Ru (Coulter, 2009)



## Comparing Ternary and Binary Films

Two foils tested under identical conditions  
Pd<sub>80</sub>Cu<sub>17</sub>Ag<sub>4</sub> and Pd<sub>88</sub>Cu<sub>14</sub> (wt.%)

T (°C)	H <sub>2</sub> /N <sub>2</sub> Selectivity		Permeability Ratio
	Binary	Ternary	
250	45	> 640	1.24
350	74	>1320	1.22
400	134	>1790	1.21

Adding a small amount of Ag appears to improve permeability of binary alloy, although observed increase is less dramatic than predicted by theory for similar compositions

Theory suggests that permeability ratio will increase as T is lowered – this is not observed in the current experiments



## Single-gas H<sub>2</sub> Permeabilities for Binary and Ternary Alloy Membranes

Membrane ID	Composition (wt%)	Hydrogen Permeability at 20 psi feed, ambient permeate (cm <sup>3</sup> (STP)-cm/cm <sup>2</sup> -s-cmHg <sup>n</sup> )				
		573 K	623 K	673 K	723 K	773 K
Pd-63	Pd <sub>75</sub> Cu <sub>25</sub>	7.05E-06	1.04E-05	1.56E-05	2.10E-05	2.81E-05
Pd-67	Pd <sub>77</sub> Cu <sub>12</sub> Pt <sub>11</sub>	1.86E-05	2.49E-05	3.44E-05	4.44E-05	5.67E-05
Pd-74	Pd <sub>73</sub> Cu <sub>12</sub> Au <sub>15</sub>	3.74E-05	5.00E-05	5.94E-05	7.26E-05	8.99E-05
Pd-95	Pd <sub>83</sub> Cu <sub>5</sub> Au <sub>12</sub>	3.99E-05	5.35E-05	6.34E-05	7.74E-05	1.40E-04
Pd-84	Pd <sub>94</sub> Ru <sub>6</sub>	4.12E-05	5.38E-05	6.47E-05	7.61E-05	9.43E-05
Pd-18	Pure Pd		7.83E-05	1.10E-04	1.07E-04	
Pd-46	Pd <sub>91</sub> Au <sub>9</sub>	7.88E-05	7.88E-05	1.20E-04	1.51E-04	1.70E-04
Pd-25	Pd <sub>85</sub> Ag <sub>15</sub>			1.35E-04		

Figure 8.9 H<sub>2</sub> permeabilities for ternary and binary palladium alloys at different temperatures compared with the permeability of pure Pd (Coulter, 2009)

### 8.7.3 Plasma Quest HiTUS system

Plasma Quest developed a sputter system called HiTUS®. This system overcomes the shortfalls of traditional sputter systems according to Plasma Quest®.

There are many technologies available to deposit the thin films required for membrane manufacture. One favored route is to use PVD, and in particular magnetron sputtering. However, this technique is limited in its ability to meet the demands of complex current and next generation membranes. Additionally, it has many shortfalls that have been shown to be readily overcome using Plasma Quest's HiTUS technology.

The stable high density plasma generated by HiTUS is done so independently of the target, which significantly opens up the sputter deposition parameter space. This enables ready tuning of the deposition parameters to optimise the thin film characteristics required of the membrane. Such optimisation enables very tight control of characteristics such as grain size, stress, density, stoichiometry and film thickness.

Plasma Quest manufactured a 2 µm thick Pd-Ag membrane with this magnetron sputtering technique. Porous SS tubes (PSS®) were covered by this 2 µm Pd-Ag film. Multiple membranes of 50 cm have been prepared (Plasma Quest, 2009).

Several membranes with a thickness of 1 µm- 5 µm were manufactured, giving an increased cost-performance benefit. Both due to the lower materials cost and the significantly higher flux obtained. Different from previous efforts they apply a two step process where the defect free Pd-alloy film is first prepared by sputtering deposition onto the extremely smooth surface of a silicon wafer. In a second step the film is removed from the wafer allowing the preparation of very thin membranes. These films may subsequently either be used self-supported or integrated with various supports of different pore size, geometry and size.

Thin Pd-Ag membranes (2 microns) have been manufactured using magnetron sputtering. The films have been applied on porous stainless steel tubes (PSS®). Multiple membranes of 50 cm

have been prepared. Plasma Quest states that the membrane performances well and has a long term stability. The results of these tests are summarised in Table 8.1.

Table 8.1 *Sputtered Pd-Ag membrane performance (Plasma Quest, 2009)*

Support	SS PSS®
Length support	50 cm
Film thickness	2 $\mu\text{m}$
H <sub>2</sub> flux	up to 2477 mL·cm <sup>-2</sup> ·min <sup>-1</sup> at dP = 25 bar (400°C)
H <sub>2</sub> permeances	between 3·10 <sup>-6</sup> - 2·10 <sup>-5</sup> mol·m <sup>-2</sup> ·s <sup>-1</sup> ·Pa <sup>-1</sup> in pure hydrogen (although 10 <sup>-5</sup> mol·m <sup>-2</sup> ·s <sup>-1</sup> ·Pa <sup>-1</sup> is extremely high)
Low pressure H <sub>2</sub> /N <sub>2</sub> permselectivity	> 7500
Maximum H <sub>2</sub> /N <sub>2</sub> permselectivity	at dP = 25 bar of 3000 (400°C)
H <sub>2</sub> permeances	up to 8·10 <sup>-7</sup> mol·m <sup>-2</sup> ·s <sup>-1</sup> ·Pa <sup>-1</sup> in WGS so far
Membrane life time	of several (2-3) years (T = 400°C) is assessed based on long-term stability tests over 250 days

## 8.8 Sputtering on porous substrates

(O' Brien, 2001) conducted magnetron sputtering of Pd-Ag membranes on porous alumina substrates. Subsequently, coatings were examined to determine the structure, pinhole density, composition, N<sub>2</sub> gas-tightness and, where appropriate, H<sub>2</sub> permeability. All coatings were found to contain pinholes. The N<sub>2</sub> gas permeance ranged from 8×10<sup>-6</sup> to 1×10<sup>-2</sup>  $\mu\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ , depending on the substrate type and condition, and H<sub>2</sub>/N<sub>2</sub> selectivity ranged from 4 to >80. The most important factor influencing pinhole formation was the initial condition of the substrate surfaces. In addition to this, some variation in composition was noted.

(Chechetto, 2004) deposited Pd thin films, 5- $\mu\text{m}$  thick, by r.f. magnetron sputtering on porous stainless steel discs (0.5  $\mu\text{m}$  rejection grade) as membrane for hydrogen filtering. The steel substrate has pore dimensions in the 20–500 nm range. In order to fill the steel pores and prepare a flat surface for the Pd coating, a polymeric layer made of commercial polycarbonate was deposited on the steel surface by spin coating technique. The PC layer shows a relatively smooth surface morphology and strong adhesion to the porous substrate. Secondary electron microscopy analysis of the fractured sample shows, in fact, branches of polymeric material which depart from the PC surface and enter in the substrate pores for length 10  $\mu\text{m}$  ensuring the necessary anchorage. Palladium sputter deposition produced rough and pinhole free Pd coating well adherent to the PC buffer layer. Gas selectivity tests by permeation analysis evidenced a hydrogen permeance of 5×10<sup>-1</sup>  $\mu\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  of the as-prepared Pd-PC composite membrane and high H<sub>2</sub> to N<sub>2</sub> selectivity, > 1000. But the selectivity dropped to approximately 10 after ten charging and discharging operations.

The result of the sputtered palladium alloy films depends on the surface conditions of the substrate. A modification of the surfaces by polishing the support was done by (Kim, 2010). The Ni support is composed of large pores and has a very rough surface. This surface offers high permeability, but leads to inhomogeneous deposition of Pd and the alloy metal on the Ni support during sputtering, see Figure 8.10 (left). As a result pinholes remain on the surface of the Pd-alloy membrane after deposition and annealing, see Figure 8.10 (left). After polishing the Pd-alloy membrane surface did not have any pinholes, see Figure 8.10 (right).

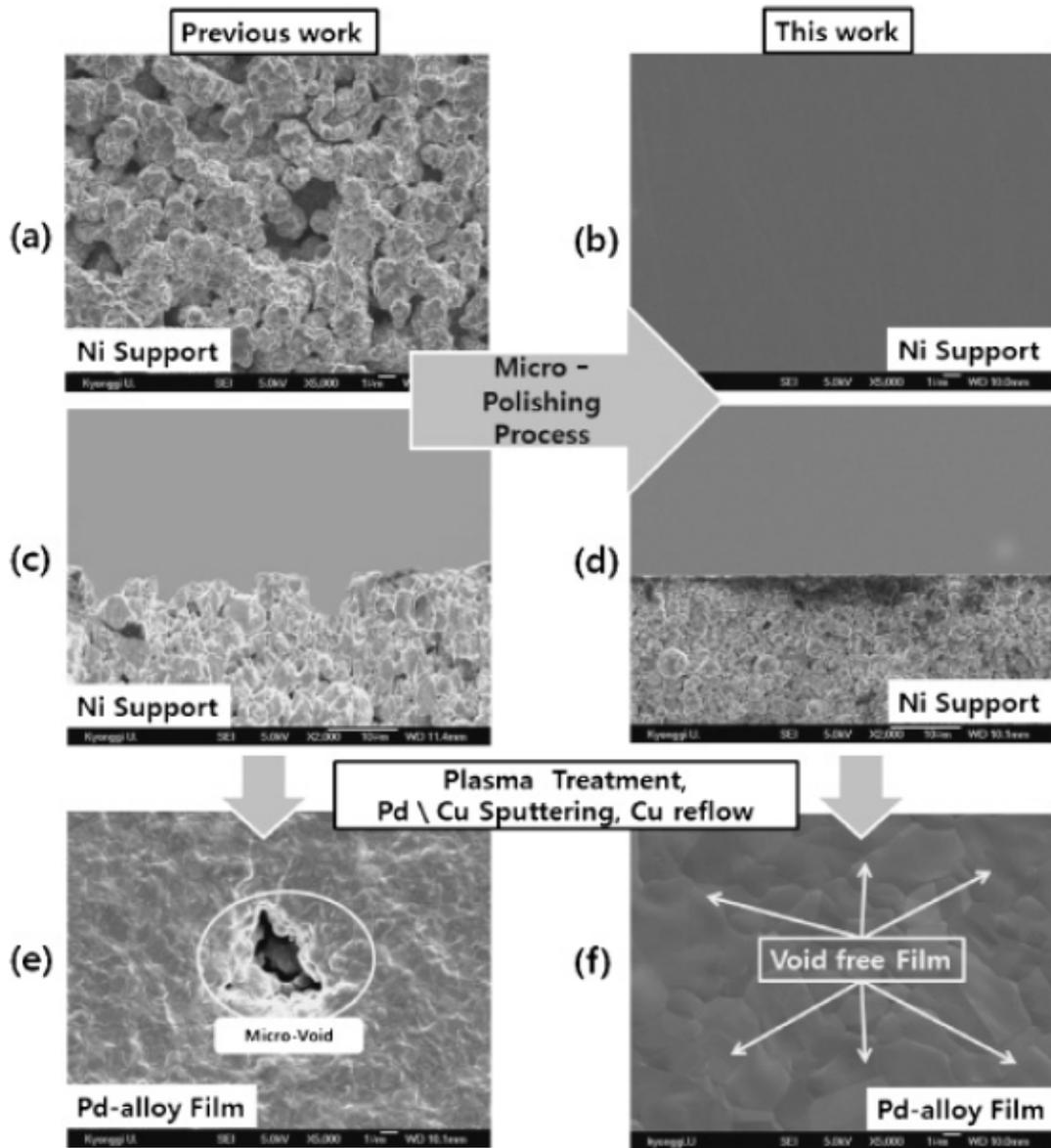


Figure 8.10 SEM photographs of the Pd-Cu film on a porous nickel support before (left) polishing and after (right) polishing (Kim, 2010)



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Version: 2010.05.31  
Classification: public

## 9. Novel techniques/ideas/alternatives

### 9.1 Electromagnetic levitation

Corus R&D developed an electromagnetic levitation technology, for high rate physical vapour deposition of coatings onto metallic strip (Baptiste, 2007).

The speed of the steel plates on which Zn or ZnMg will be plated by the standard Zn and MgZn deposition techniques is between 2-3 m/s. The layer thickness is in the order of 7  $\mu\text{m}$ .

Based on private communication with Bart van Velthuisen (group leader R&D galvanising): "The plate speed in the order of 2-3 m/s for the new electromagnetic levitation pilot plant. Zn and aluminium layers of the order 3-4  $\mu\text{m}$  are deposited".

In principle this technique can be used for palladium alloy deposition. But it is expected that the deposition rate for palladium alloy with components like Ag, Cu to be low. This is due to the vapour pressure versus temperature character. Zn vapour pressure is approximately 1 bar at a temperature, like 900°C. The vapour pressure for Pd, Ag and Cu are much lower. This requires a higher temperature like approximately 2600°C for Cu and approximately 3100°C for Pd

The slit size is critical in this process. The morphology has to be optimised for the palladium alloy deposition. Corus does not have any knowledge available in depositing palladium alloys with this technique because the core business is deposition of Zn or Al on steel plates.

Data on the pinhole or defect density of the deposited layers in this process is confidential but will be low since corrosion protection is the aim.

### 9.2 Electro deposition ionic liquids

The deposition of a binary or ternary alloy from some electrolyte is challenging. Ionic liquids are a relatively hot field of science. Electro deposition is most frequently done in aqueous solutions. In ionic liquids the solvent is not an aqueous solution but a molten salt. The limitations of aqueous solutions are:

- limited potential window,
- gas evolution processes; hydrogen embrittlement,
- passivation of metals can cause difficulties,
- necessity for complexing agents like cyanide.

These problems can be solved with ionic liquids.

Several Pd-Ag, Pd-Au and Pd-In were electrodeposited from ionic liquids. XRD measurements indicated that the alloys were solid solutions of Pd-Au and Pd-Ag (Endres, 2008).

Electrodeposition of palladium silver alloys from an ammoniacal electrolytes (Sturzenegger, 1984). A potential problem is the ventilation that is required because a large amount of ammonia is present in the plating bath.

### 9.3 Electrochemical based cleaning

Cleaning of extrusion dies for aluminium extrusion is often done by using alkaline hot baths. The steel extrusion dies are immersed in these baths. The alkaline solution dissolves the aluminium without attacking the steel. This method can be used as follows:

- prepare thin foil aluminium tubular supports,
- sputter palladium alloys on these supports,
- dissolve the aluminium preferentially without attacking the thin palladium alloy film,
- electrochemical enhanced dissolving of the aluminium foil is also possible.

In the end a palladium alloy tube is left.

### 9.4 Replacing Pd

The production of high purity hydrogen is an important technical issue, which is related to future energy and environmental problems. Membranes of palladium alloys have been used commercially for decades to provide high purity hydrogen mainly for laboratory use and semiconductor manufacture. Another idea for reducing the costs of palladium alloy materials for large-scale production of high purity hydrogen is replacing Pd for another metal. Some vanadium-based alloys for membrane materials have been developed to purify hydrogen gas to replace palladium (Nishimura, 2009)

## 10. Performance of Pd alloy membranes for different manufacture routes

(Tosti, 2002) compared palladium-ceramic membranes that were produced by three different routes. Three techniques were used to produce palladium–ceramic (Pd–ceramic) composite membranes for hydrogen separation and production. These are sputtering, electroless deposition and rolling of thin Pd alloy films over ceramic porous tubes.

After studying and developing the three coating techniques, extensive testing and characterising work was carried out on these thin film composite membranes. The results show that in the sputtered (0.5–5  $\mu\text{m}$ ) and electroless deposition (2.5–20  $\mu\text{m}$ ) composite membranes, the thermal cycling of the hydrogenated metallic layer produces membrane failures. Such failures are characterised by crack formation and metal film peeling. This fact has been explained by an evaluation of the shear stresses at the metal–ceramic interface due to the different thermal expansion coefficient of palladium (Pd) and the ceramic support under thermal cycling and hydrogen loading. The rolled membranes (50–70 $\mu\text{m}$ ), however have shown a complete hydrogen selectivity and good chemical and physical stability in long-term tests.

An overview of test results of thin film palladium alloy membranes prepared by different manufacturing routes is summarised in Table 10.1. For more details of the results in Table 10.1 is referred to (Mallada, 2008). A direct comparison of these results which manufacture route results in the best membrane performance is difficult due to the differences in experimental conditions.

Table 10.1 Permeation and selectivity data of different palladium based foils reported in the literature at various testing conditions. The references are presented in (Mallada, 2008)

Membrane type	T [K]	$\Delta P$ (kPa)	Thickness [ $\mu\text{m}$ ]	$\text{Flux}_{\text{H}_2}$ ( $\text{mol}/\text{m}^2\text{s}$ )	$P_{\text{eff}}$ ( $\text{mol}/\text{m}^2\text{s Pa}$ )	$\alpha_{\text{H}_2}/\alpha_{\text{N}_2}$	$E_{\text{H}_2}$ (kJ/mol)	$P_0$ ( $\text{mol}/\text{m}^2\text{s Pa}^{0.5}$ )	Preparation method	References
Pd-ZrO <sub>2</sub> -PSS	773	100	10	0.083	$8.3 \times 10^{-24}$	—	7.1	0.6	ELP	[56]
Pd- $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	573	290	1	2.05	$3.8 \times 10^{-34}$	$10^{-6}$	—	—	MCVD	[57]
Pd-Al <sub>2</sub> O <sub>3</sub>	723	—	4.8	—	$3 \times 10^{-6}$	60	—	—	ELP	[58]
Pd/Ag-Al <sub>2</sub> O <sub>3</sub>	—	142	10	0.142	$1 \times 10^{-64}$	1500	—	—	ELP	[59]
Pd/Ag-PSS	723	1000	29	—	—	8	—	—	ELP	[60]
Pd-PSS	593-773	—	20	—	—	—	12.54	56.41	ELP	[61]
Pd-Al <sub>2</sub> O <sub>3</sub>	573	30	2-4	0.1-0.2	$6.66 \times 10^{-64}$	5000	—	—	CVD	[34]
Pd-GCM	473	10	15	0.223	$2.23 \times 10^{-50}$	7	—	—	ELP	[43]
Pd-Al <sub>2</sub> O <sub>3</sub>	801	—	2-3	—	$1.162 \times 10^{-6}$	<18	—	—	ELP	[62]
Pd/Ag-PSS	673-773	162	50	—	—	8	33.31	$1.66 \times 10^{-3}$	LT	[63]
Melt-Spun Zr-Al-Co-Ni-Cu	673	390	44	0.0044	$1.13 \times 10^{-60}$	—	—	—	MST	[64]
Pd alloy/PNS	773	358	—	0.083	—	3.7	—	—	MST	[65]
Pd-Cu alloy	725	—	0.75	1.6	—	500(H <sub>2</sub> /He)	—	—	DST	[66]
Pd/Ni	673	20	2.5	0.31	$1.15 \times 10^{-54}$	—	—	—	DC SP	[67]
Pd/Ag alloy	620	400	5.5	—	$10 \times 10^{-7}$	>4500	9.8	—	SELP	[68]
Pd/MPSS	773	100	6	0.302	$3.02 \times 10^{-60}$	—	16.7	—	ELP	[69]
Pd	473	51	95	0.0267	$5.235 \times 10^{-77}$	—	23.16	—	Oxidation	[70]
Pd <sub>81</sub> -Cu <sub>19</sub> /ZrO <sub>2</sub> -PSS	753	250	5	0.6	$5.265 \times 10^{-47}$	8	14.5	—	ELP	[71]
Pd/PSS	773	100	11.7	—	$7.91 \times 10^{-4}$	—	—	—	—	[72]
Pd <sub>90</sub> -Ag <sub>10</sub> - $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	473-616	80-250	20	0.14	$1.25 \times 10^{-64}$	30-178	—	—	ELP	[73]
Pd-CS	623-773	400	2	—	$1.688 \times 10^{-6}$	1140-12900	12.19	144.6	ELP	[74]
Pd/Pd-Ag-PSS	673-773	100	2-3	0.3	$3 \times 10^{-64}$	—	25.7	0.17	ELP	[31]
Pd-Ag/ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /PSS	773	100-500	16-20	—	$4.91 \times 10^{-4}$	3500-5000	—	—	SELP	[75]
Pd-Cu/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	723	345	11	0.8	$2.31 \times 10^{-60}$	1150	—	—	ELP	[76]
Pd/TiO <sub>2</sub>	773	45	0.3-0.4	0.283*	$6.28 \times 10^{-64}$	1140	—	—	ELP-UV	[77]
Pd-Ni/SS	623-823	68	0.8	0.138-1.315	$2.02 \times 10^{-64}$ $-1.93 \times 10^{-59}$	300-4700	—	—	VED	[78]
Pd-Ru-In/SS	645	100	1.5	0.049	$4.9 \times 10^{-74}$	8	—	—	SD	[79]
Pd-Al <sub>2</sub> O <sub>3</sub>	673	100	5	0.155	$1.55 \times 10^{-64}$	100-200	—	—	ELP	[80]
Pd/PSS	793	150	10	0.175	$1.166 \times 10^{-67}$	—	—	$8.862 \times 10^{-4}$	ELP	[81]

\*Calculated from reference data.

(Lu 2007) reviewed different production techniques for the manufacture of inorganic membranes for hydrogen separation. He concluded that there are generally three techniques for coating metallic thin films onto porous metallic or ceramic supports: electroless plating, chemical vapour deposition (CVD) and physical sputtering. Under controlled conditions all three methods produce good quality membranes with high hydrogen selectivity over 3000 at temperatures above 300°C.

The electroless plating technique is a simpler and often more effective method of preparation which has a number of advantages such as uniformity of coatings on complex shapes, high coating adhesion, low cost, equipment and operation simplicity. The CVD method also has the advantages of the flexibility to coat metal films on support of different geometry. The main disadvantage of these two chemical methods is the difficulty to control the composition of metal alloy deposited. As a consequence sputtering is then more versatile with respect to the alloy composition control.

DC or RF sputtering method of depositing Pd and its alloys, however, is found to produce very thin Pd/Ag membranes of good quality (McCool, 1999). Although the substrate surface conditions are very important for producing good quality, pinhole free Pd and Pd-alloy membranes.

That does not mean that the electroless plating technique is not useful. The osmosis electroless plating technique was used for the repair of pinholes and defects in a Pd/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> composite membranes, which originally contained a large number of defects (Li, 2000).

In terms of the microstructure of the thin films produced, the following summarises the different features of the products by three different methods (Lin, 2001):

- Thin Pd/Ag membranes prepared by the electroless plating tend to contain large crystallites (in submicron range) and is polycrystalline.
- The CVD metal membranes can be polycrystalline or nanocrystalline with a grain size of the order of several hundred nm, depending on the deposition conditions.
- Those by the sputtering deposition are nanocrystalline with crystallite sizes in the range of 20–100 nm.

According to (Lu, 2007) there are many discrepancies in the literature on hydrogen permeation data through various thin Pd/Ag membranes prepared by different methods. This can not only be explained by the differences in membrane thickness and composition. The microstructural effects (e.g., the crystallite size) on the hydrogen permeation is possibly also of importance. Processes like bulk diffusion versus grain boundary diffusion depends on the crystallite size.

(Lin, 2001) examined the effects of the grain size on hydrogen permeation for 200 nm thick Pd/Ag films prepared by sputtering. The films were annealed at 600°C for grain growth. The hydrogen permeation through the membrane before and after the grain growth was measured and are presented in Figure 10.1. The result in Figure 10.1 show that an increased crystallite size results in an increased hydrogen permeance. This effect is enhanced at higher temperatures and points at bulk diffusion. These data clearly indicate the importance of nanostructure (thus deposition method) of the Pd–Ag film on hydrogen permeance.

Clearly, there is wide variation in the values reported for the permeability data depending on the porous substrate, coating methods used. Generally, the permeabilities of Pd supported membranes follow the order: Electroless deposition > CVD deposition > sputtering method (Lu, 2007).

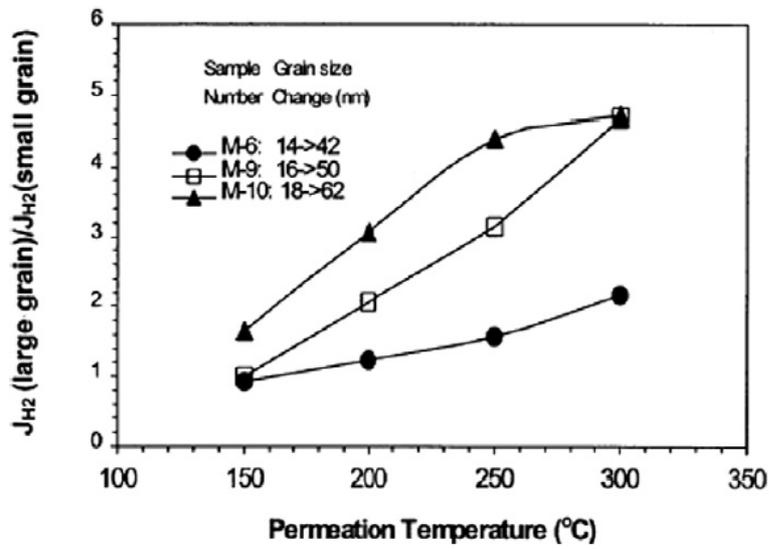


Figure 10.1 *Ratio of hydrogen permeance after grain growth to that before the grain growth for three different nanocrystalline Pd-Ag membranes of 200 nm thickness prepared by sputtering (Lin, 2001)*

## 11. Discussion: Summary of the results

Several requirements are presented in Chapter 2. This paragraph gives a summary in which the requirements are presented per film forming or deposition technique. In this way a list can be formed where a ranking of the most versatile and most promising film forming or deposition technique can be selected.

Thin film/foil techniques for polymer based substrates like film blowing extrusion are not further included. These techniques are not suitable for metals due to differences in mechanical/flow behaviour. Atomic layer deposition is also rejected as a suitable technique because of the very low layer growth rate. Chemical vapour deposition techniques are also rejected because there is a limited amount of feasible precursors.

The following requirements and properties are compared:

- layer growth or deposition rate,
- possibility formation binary, ternary or multicomponent (more than three alloying elements) alloy,
- thickness uniformity large scale,
- pinhole formation,
- number of steps to end product,
- industrial application areas and scale,
- microstructure,
- performance hydrogen permeance,
- thermal cycling behaviour,
- robustness.

*Layer growth or deposition rate*

Techniques	Rate	Remarks
Rolling	Very high	Long processing time. Depends highly on required thickness. Lower thickness more heat treatment steps
Drawing	Very high	Thickness limitation of 20 $\mu\text{m}$
Chemical thinning	No information	Etching agents determine the "corrosion rate". Also dependent on starting thickness of the foil
Laser assisted	6000 $\mu\text{m}/\text{h}$	Industrial scale $\rightarrow$ mechanical treatment afterwards done. The minimal layer thickness is relatively high (above 100's of $\mu\text{m}$ )
Pulsed laser deposition	0.0360 $\mu\text{m}/\text{h}$	0.001 – 1 $\text{\AA}$ per pulse Small scale areas. Depends on laser technology: pulse rate, total power
Thermal spraying	600 - 6000 $\mu\text{m}/\text{h}$	Thick layers (> 50 $\mu\text{m}$ ) required for pinhole free
Sputtering	1 $\mu\text{m}/\text{h}$ – 10 $\mu\text{m}/\text{h}$	SINTEF Si wafer & SwRI web coater
Electroless plating	2 - 5 $\mu\text{m}/\text{h}$	
Electroplating	1- 5 $\mu\text{m}/\text{h}$	

*Formation binary; ternary alloy or multicomponent alloys*

Techniques	Binary/ternary or more elements	Remarks
Rolling	Yes	Deformation or flowing behaviour during rolling highly dependent on alloy composition. No information found yet on mechanical data from Pd-Ag-Au-X-X material
Drawing	Yes	Flowing behaviour during drawing highly dependent on alloy composition. No information found yet on mechanical data from Pd-Ag-Au-X-X material
Chemical thinning	Depends on etching agent/composition	Depends on microstructure → local higher etching rates
Laser assisted	Maybe	Depends on possibility of making fine powders with alloy content.
Pulsed laser deposition	Yes	Different targets available
Thermal spraying	Maybe	Depends on possibility of making fine powders with alloy content.
Sputtering	Yes	Different targets available. Fine tuning deposition rates. In principle no limitations except thermodynamics. Feasibility ternary alloys by SwRI (PdCuAu, PdCuPt). Versatile deposition technique
Electroless plating	Maybe (used for Pd-Ag and Pd-Cu)	Depends on bath chemistry knowledge development. Deposition of an alloy is difficult. Very long heat treatments afterwards are required.
Electroplating	Maybe	Depends on bath chemistry knowledge development. Deposition of an alloy is difficult. Heat treatment afterwards required

*Risk pinhole/defects formation (selectivity)*

Techniques	Pinhole formation	Remarks
Rolling	Increasing pinhole density at thickness reduction in the range below 20 $\mu\text{m}$	Maximum width 2020 mm for 6 $\mu\text{m}$ Al foil. Maximum width 150 mm for < 20 $\mu\text{m}$ Pd foil. Only rolling followed by chemical thinning results in $\mu\text{m}$ thickness palladium alloy foil.
Drawing	Pinhole free	Wall thickness of 10 - 20 $\mu\text{m}$ are the limit. But this is only possible for small radius tubings.
Chemical thinning	HY9 states pinhole free foils	Starting with 20 – 25 $\mu\text{m}$ thick foil. After chemical thinning thickness reduction to 8 $\mu\text{m}$ foil.
Laser assisted	Yes	Very large content; porous layer.
Pulsed laser deposition	Yes/Possible	No information on exact pinhole size.
Thermal spraying	Yes (decreasing tendency with thickness)	Also a porous layer is formed. Pd layer with HVOF with a thickness > 50 $\mu\text{m}$ was pinhole free. Another disadvantage is that the deposition efficiency is not 100%. Material loss will result in higher costs.
Sputtering: direct	Low to none	The most important factor influencing pinhole formation was the initial condition of the substrate surfaces. Porosity of the support is an issue. Preparations like filling of the pores and micro polishing of the membranes will result in pinhole free palladium alloy films. Checchetto claims high selectivity after PC pore plugging Checchetto; Pd, 5- $\mu\text{m}$ thick, stainless steel discs pores dimension 20–500 nm range. High selectivity? (not quantified)
Sputtering: free standing	Very low to none	Highly dependent on support surface quality. Surface treatment procedures from vacuum coating technology used for pinhole free foil production.
Electroless plating	Low	Porosity of the support is an issue. Preparations like filling of the pores and micropolishing of the membranes will result in pinhole free palladium alloy films. On lab scale pinhole free production. Large scale thickness control an issue.
Electroplating	Yes (thickness dependent)	Large scale chrome and nickel plating experience shows that pores will still form.

*Thickness uniformity large scale*

Techniques	Thickness uniformity large scale	remarks
Rolling	Yes	Precision rolling technology dependent. Expected below 5%.
Drawing	Yes	Within 7% is possible.
Chemical thinning	Depends on etching agent/composition	
Laser assisted	Very thick layers/porous	Above 5 $\mu\text{m}$ thickness still porous layers.
Pulsed laser deposition	Yes for large scale samples in pulsed layer deposition	Sample size of the order of 10 cm in diameter
Thermal spraying	Very thick layers	Above 50 $\mu\text{m}$ HVOF coated Pd layer.
Sputtering: direct	Yes	Lower than 5% in thickness variation is possible.
Sputtering: free standing film	Yes	Lower than 0.9 % in thickness variation.
Electroless plating	No	Keeping local constant bath homogeneity is a problem.
Electroplating	No	Sharp edges/corners increased deposition rates.

*Steps to end product*

Techniques	Approximated steps	Remarks
Rolling	5	Foil rolling – cutting – forming/sealing/heat treatment.
Drawing	3	Free standing tube over support → sealing/heat treatment.
Chemical thinning	6	Foil rolling - chemical etching - foil – cutting – forming/sealing/heat treatment.
Laser assisted: cladding	3	Support surface pre-treatment - cladding – heat treatment.
Pulsed laser deposition	3	Support surface pre-treatment - deposition – heat treatment?
Thermal spraying	4	Support surface pre-treatment - deposition – heat treatment -- mechanical treatment?
Sputtering: direct	3	Support surface pre-treatment (pore plugging) – sputtering – heat treatment.
Sputtering: free standing film	7	Carrier support surface pre-treatment – sputtering - remove carrier free standing film – "cutting" – forming/sealing/heat treatment
Electroless plating	> 14 (sequential deposition, for binary alloy)	Support surface pre-treatment – several steps (7) per alloy element (different baths required for co-deposition) – heat treatment
Electroplating	> 7 (binary alloy)	Support surface pre-treatment – several steps (different baths required for co-deposition) – heat treatment

*Industrial application areas and scale:*

Techniques	Industrial	Remarks
Rolling	Yes	Aluminium foil. Mature technology for large scale. PdCu in foil form available (Kellogg, 2010).
Drawing	Yes	The thickness to diameter ratio is very exceptional. It is not impossible but no large scale manufacturer was found in this area.
Chemical thinning	Semi–small scale (width 20 cm; length depends on foil roll length)	Hy9 planar membranes; Etching bath issues; health/environment issues.
Laser assisted	Yes	Cladding of wear, corrosion resistant layers on machine parts.
Pulsed laser deposition	Semi—small scale (10 cm substrates)	High vacuum required. High temperature superconductors. Sample size ranges from 10 cm diameter (row by row) to 3 cm width and meters length.
Thermal spraying	Yes	Very large areas; Generic technology for metallising. HVOF Pd coating on substrate was found in literature. But requires very thick coatings in order to have no pinholes.
Sputtering: direct	Yes	Vacuum and cleaning procedures required. Leybold optics: 3D sputtering coater 1.2 m height. HEF 2.1 m long vacuum chamber. At the moment no 3 m long vacuum are available. End result highly dependent on the surface condition of the support. Technologies available that can improve the surface finish quality of the support such that the direct sputtered palladium alloy film are pinhole free or have very low amount of pinholes.
Sputtering: free standing film	Yes	Vacuum and cleaning procedure required. Roll-to-roll, vacuum web coating technologies. Applied materials, Leybold optics, Plasma Quest and other vacuum coating equipment builders do have working systems. SINTEF and Plasma Quest manufactured 50 cm long pours support membranes.
Electroless plating	Yes mono-metal	Only large scale electroless palladium plating was found in semi-conductors/electronics industries. ENEPIG process in the printed circuits board industry. ECN prepares 9 decimetres long pure palladium membranes. Health/environment issues; control of bath chemistry very critical. End result highly dependent on bath stability and amount of pollution in bath.
Electroplating	Yes mono-metal	Health/environment issues; Control bath chemistry critical; End result highly dependent of sample surface morphology, stirring and amount of pollution in bath. Technochrome, DMI; Nickel and Chrome plating processes on a large scale. No large scale electroplating of palladium and palladium alloys was found in literature.

*Microstructure*

Techniques	Microstructure	Remarks
Rolling	Long grains Small grains after heat treatment	
Drawing	Similar as for rolling	
Chemical thinning	Similar as for rolling	
Laser assisted	Solidified alloy. No equilibrium conditions	Depends on substrate temperature
Pulsed laser deposition	Sintered structure with pores	Depends on substrate temperature
Thermal spraying	Sintered structure with pores	Depends on substrate temperature
Sputtering	Nanocrystalline 20-100 nm	Heat treatments can improve the microstructure.
Electroless plating	Submicron scale crystallites	Annealing treatment needed to form an alloy. Heat treatments can improve the microstructure
Electroplating	Expected similar as for electroless	Annealing treatment needed to form an alloy. Heat treatments can improve the microstructure

### *Performance*

A direct comparison of these results which manufacture route results in the best membrane performance is difficult due to the differences in experimental conditions that are used in the many references in the available literature.

Techniques	Permeability	Selectivity
Rolling	(references in Guazzonne, 2005)	(references in Guazzonne, 2005)
Drawing	No data	No data
Chemical thinning	No data	No data
Laser assisted	No data	No data
Pulsed laser deposition	No data	No data
Thermal spraying	Data available (Hollein, 2001)	Data available (Hollein, 2001)
Sputtering	Between $3 \cdot 10^{-6}$ - $2 \cdot 10^{-5}$ mol·m <sup>-2</sup> ·s <sup>-1</sup> ·Pa <sup>-1</sup> in pure hydrogen	> 7500
Electroless plating	See variation in Table 10.1. On average slightly higher than for sputtering (Lu, 2007)	See variation in Table 10.1.
Electroplating	See variation in Table 10.1 from (Mallada, 2008).	See variation in Table 10.1 from (Mallada, 2008)

### *Thermal cycling/robustness*

Long term stability/robustness are two important factors. In general there is limited data in the available literature on the subject of thermal cycling and robustness. This lack of data is confirmed by (Lu, 2007). (Westerwaal, 2010) reviewed this topic in more detail.

SWRI found that failure of the thin film membranes occurred primarily on the seals of their testing equipment for the membranes (Coulter, 2008). SWRI is focussing at testing conditions for industrial applications. It is expected that long term cycling test data will be published in future.

Sintef found that the long term behaviour of their Pd-Ag membranes on a PSS support failed due to interdiffusion phenomena (Peters, 2008). After this improvement Pd-Ag membrane failure still occurred, but this was due to the membrane seals.

Techniques	Thermal cycling	Remarks
Rolling	No data	Expected that thick membranes will have a longer life time.
Drawing	No data	Expected that thick membranes will have a longer life time.
Chemical thinning	No data	No data available in our range of interest (Kellog 2010).
Laser assisted	No data	
Pulsed laser deposition	No data	Limited area can be manufactured by this technique
Thermal spraying	No data	
Sputtering (free standing film)	Pd-Ag on PSS support expected life time 2-5 years At $T \leq 425^{\circ}\text{C}$ based on 100 days performance testing (Peters, 2009) Pd-Cu system tests still evaluated (Morreal, 2009)	An interdiffusion barrier layer must be present to increase temperature stability (Peters, 2008). Pinholes develop during the 100 days testing period without a interdiffusion barrier layer. PdAg film of approx. $190 \text{ cm}^3$ at 50 cm support length (Peters 2008)
Electroless plating	Pd-Ag on ceramic support, 100 days performance tests (Delft, van, 2009) Pd-Cu on ceramic support withstood 30 temperature cycles between room temperature and 673 K (Goldbach, 2010)	Pinholes form, possibly due to coexistence of amounts of fcc phase (Golbach 2010))
Electroplating	No data	No option on insulators

## 12. Conclusions

1. Sputtering is the most versatile technique for the production of thin film palladium alloy membranes on a large scale.
  - Magnetron sputtering mode for deposition of a fixed alloy composition.
  - Co-sputtering with several magnetron targets for flexibility in membrane alloy composition.
2. Deposition techniques using dissolved reactants like electroless and electro deposition are less suitable for the production of binary, ternary and multicomponent palladium alloys due to difficulties in controlling the alloy composition and layer thickness on large areas.
  - Chemical thinning process is limited in its applications to PdCu foils.
3. Pulsed laser and laser assisted processing can not be used for the deposition of palladium alloys on large areas.
4. Rolling is limited in its use due to: pinhole formation at reduced foil thickness ( $< 6 \mu\text{m}$ ), dependence on formation of brittle phases in the foil and the availability of palladium alloys having the proper chemical composition in the form of foils.
5. Drawing is no option for the manufacturing due to the tube diameter to membrane thickness ratio.
6. Thermal spraying is no option due the high thickness of  $> 50 \mu\text{m}$  to produce defect free films

### 13. Recommendations

Several industrial parties are working in the field of sputter deposition and some preliminary discussions have been initiated. Extended discussions and collaborations are necessary to assess the full potential for large scale sputter-based deposition of Pd-alloy layers on porous substrates for hydrogen-selective membrane manufactory. Also an in-depth investigation of available sputtering techniques is required. Special attention have to be paid to parameters such as: temperature, pressure, comparison of 2-D sputtering configuration (x-y substrate or target movement) versus 3-D (x-y-z substrate or target movement) sputtering configuration on the deposited Pd-alloy layers on porous substrates.

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