

PREPARATION OF PALLADIUM-SILVER ALLOY MEMBRANES FOR HYDROGEN PERMEATION

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Abstract— Pd-Ag alloy membranes (with different silver contents) have been prepared by electroless plating technique for hydrogen separation. The surface morphology and phase structures of the composite membranes were investigated using a scanning electron microscope and a X-ray diffractometer, respectively. Hydrogen permeation experiments through the membranes synthesized at different hydrogen pressures (50 – 250 kPa) and temperatures (623 – 823 K) are reported. The experimental results reveal that the membranes showed a considerable enhancement in the hydrogen permeation and that the contribution of surface process for permeation was significant at high temperatures.

Key words – Membrane preparation, palladium-silver, hydrogen permeation.

I. INTRODUCTION

Hydrogen selective membranes are important for technological process such as separation and recovery of hydrogen from process steam reforming, purification of hydrogen for fuel cell application and chemical reactions in membrane reactors (Chai *et al.*, 1995; Kikuchi, 1995; A.-Petersen *et al.*, 1998; Wieland *et al.*, 2002; Kusakabe *et al.*, 2005). Palladium membranes have been used in hydrogen separation because present high selectivity (Tosti *et al.*, 2003; Checchetto *et al.*, 2004). However, they present problem of hydrogen embrittlement, a phenomenon in which dissolved hydrogen tend to cause different elongation of metallic film on glass support, leading it to fracture after repeated pressure and thermal cycling (Tosti *et al.*, 2001). In order to avoid the embrittlement, alloying of Pd with group IB metals such a silver is generally made. (Fort *et al.*, 1975). Another advantage of alloying is that the mechanical strength can be higher than for pure palladium. In general, a Pd-membrane becomes brittle after certain cycles of α - β hydride transformations due to the accompanied lattice expansion. In, for example, palladium-silver alloys, the lattice has already been expanded by the silver atoms, and the PdAg lattice is less influenced by hydrogen and thus less brittle than the pure Pd lattice (Amandusson *et al.*, 2001). A optimal value of the hydrogen permeation rate is reached for a silver content around 25 wt. % Ag (Knapton, 1977; Uemiya *et al.*, 1991). Zhang *et al.* (2003) had observed that at 473 K or less, the hydrogen permeability of Pd-Ag alloy membranes increased with the Ag content until 30 wt. %. Other alloys like cerium-palladium, palladium-tantalum, palladium-niobium,

yttrium-palladium and copper-palladium showed high permeability and mechanical strength (Fort *et al.*, 1975; Buxbaum and Kinney, 1996; Roa *et al.*, 2003; Siriwardane *et al.*, 2003; Howard *et al.*, 2004; Tong *et al.*, 2006). There are various methods reported in the literature for fabrication of composite Pd-based membrane for hydrogen permeation such as chemical vapor deposition (Xomeritakis and Lin, 1998; Jun and Lee, 2000; Itoh *et al.*, 2005), sputter deposition (Jayaraman *et al.*, 1995; Jayaraman and Lin, 1995; McCool, *et al.*, 1999), electroless plating with osmosis (Souleimanova *et al.*, 2001; Souleimanova *et al.*, 2002) and electroless plating (Tong *et al.*, 2005; Lin and Chang, 2005; Tanaka *et al.*, 2005; Rahimi and Iraj, 2005), being this last more used for having as advantages low cost and the use of very simple equipment (Altinisik *et al.*, 2005).

The goal of this work was to prepare palladium-based membranes with different silver contents, in order to investigate the influence of Ag concentration on hydrogen permeation. Characterization studies of Pd-Ag alloy membranes were performed using SEM and XRD.

II. METHODS

Porous Vycor glass tube (Corning Glass, Inc.) was employed as support for the manufacturing of Pd-Ag alloy membranes. The specifications of the support are: length of 10 cm, outer diameter of 10 mm, inner diameter of 7 mm and average pore size of 50 Å. The porous tubes were first cleaned with hydrogen peroxide, trichloroethylene and deionized water as procedure described by Cheng and Yeung (1999). Following the cleaning, a procedure with palladium predeposition was performed before co-deposition of Pd-Ag by method electroless plating. Initially, the support was seeded with Pd crystallites that formed nucleation sites for subsequent plating of a Pd-Ag film on the substrate. This process involved immersion of the substrate in SnCl₂.2H₂O 5mM solution for 5 min followed by another 5 min in PdCl₂ 5mM solution. This sequence was repeated 9 times. Afterwards the palladium and silver deposition was carried out at 323 K, for 60 min in a plating bath containing a 70 mL solution with composition listed in Table1. After the plating the membrane was washed with deionized water and allowed to air dry. The total amount of metals in plating solution was kept constant at 0,911 mM, however the content of palladium and silver was altered in order to form a metallic film on the membranes with different silver contents. After the plating, the samples were sintered at 823 K in a pure hydrogen atmosphere for 3 h to promote alloying.