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Effect of surface roughness and mass transfer enhancement on the performance characteristics of nickel-hypophosphite electroless plating baths for metal–ceramic composite membrane fabrication

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ABSTRACT

Mass transfer enhanced electroless plating is a relatively new concept in the field of metal–ceramic composite membrane fabrication. In this article, we present the effect of substrate surface roughness along with various mass transfer enhancement techniques such as solution stirring, membrane stirring and sonication on metal conversion, plating efficiency, thickness, and percent pore densification using electroless plating of nickel on a porous disk shaped ceramic support with a nominal pore size of 700 nm. The plating characteristics were investigated for three different roughness values, stirrer speeds (0–300 rpm) and a loading ratio (defined as membrane area per unit volume of plating solution) value of 196 cm^2/L. It was evaluated that stirring as well as sonication had a profound effect on sodium hypophosphite based electroless nickel baths. This led to a reduction in average membrane pore size by 100 nm for stirring and 130 nm for sonication when compared to the base case. Surface roughness was observed to influence the metal deposition characteristics for base case without mass transfer enhancement. Sonication, irrespective of surface roughness, provided the maximum values of selective conversion, densification and membrane thickness along with acceptable values of plating efficiency.

Keywords: Nickel membrane; Electroless plating; Stirring; Ultrasound; Surface roughness; Sodium hypophosphite

1. Introduction

Amongst several techniques for metal–ceramic composite membrane fabrication, electroless plating is prominent due to numerous advantages such as low cost, easy to build and scale up, ability to deposit metal on complex shapes. The traditional electroless plating process for metal–ceramic composite membrane fabrication involves the deposition of desired metal (such as palladium) on the seeded support using solutions prepared with metal precursors, reducing agents and stabilizers. Amongst several reducing agents, hypophosphite and hydrazine received considerable attention as reducing agents to deposit palladium metal on membrane supports. Nonetheless electroless plating is a slow process that has severe mass transfer limitations and in the recent times, few authors investigated on mass transfer coupled electroless plating process for metal–ceramic membrane fabrication (Ayturk and Ma, 2009; Bhandari and Ma, 2009; Zhang et al., 2008).

One of the primary objectives for palladium–ceramic membrane fabrication is to achieve near 100% pore densification to achieve a defect-free dense membrane for applications in separations and in membrane reactor devices. In addition, dense metal film stability at high operating temperatures is also of primary concern. To achieve a high degree of metal densification, engineering the ceramic support is usually targeted. Amongst several possibilities, usually asymmetric support membrane morphology is targeted using materials such as γ-alumina, chromia (Samingprai et al., 2010) zirconia (Gao et al., 2005) which can also act as intermetallic diffusion barriers. On the other hand, tradeoffs are associated with the surface roughness of the membrane support. While a smoother

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membrane surface enables achievement of dense metal–ceramic membrane with minimal metal film thickness, its higher temperature stability is anticipated to be low. This is due to the fact that the adhesion of metal film to a smoother surface will not be as strong as the adhesion of the metal film to a rougher surface. On the other hand, supports with rougher surfaces will require higher metal film thickness to achieve near 100% densification but do possess better capabilities to withstand temperature cycling phenomena. All in all, it can be observed that surface roughness is an important parameter in the engineering of metal–ceramic composite membranes.

Literatures pertaining to the effect of surface roughness on metal plating deposition characteristics during metal composite membrane fabrication are scarce. From several studies conducted for Pd-stainless steel dense membrane fabrication using electroless plating, Lin and Chang (2005) opined that lower metal deposition rates exist for lower skin layer roughness. However, their study did not involve a variation in the support surface roughness. Huang and Dittmeyer (2006) further validated the earlier hypothesis for the associated tradeoffs. The authors inferred that dense palladium membranes prepared using atmospheric plasma spraying with yttria-stabilized zirconia skin layer had to be significantly thicker (15–20 μm) when compared to the membranes prepared using wet powder spraying and titania skin layer (8–10 μm). This is due to the reason that the former membrane had extremely rough-surface. However, the adhesion of palladium membrane to the TiO_2 surface was found to be not satisfactory, as the composition of titania was observed when the membrane was exposed to hydrogen at higher temperature. Chi et al. (2010) reported the fabrication of a dense palladium composite membrane with a Pd metal layer of 4.4 μm on a stainless steel support modified with alumina oxide particles for both support pore size and roughness reduction. However, quantitative information with respect to the reductions in support pore size and roughness were not presented.

Few other literatures that did not target metal–ceramic membrane fabrication addressed the effect of surface roughness on the performance of electroless plating process. Liu and Gao (2006a) observed that higher deposition rates and higher coating adhesion was observed when a roughened AZ91 Mg substrate was used for electroless plating of Ni. Similarly, Meenan et al. (1994) opined that Pd growth was proposed to depending strongly on surface roughness during the electroless deposition over tungsten oxide films and smooth surfaces lead to a uniform distribution. Ranjbar et al. (2010), Zhao et al. (2007) and Liu and Gao (2006b) also indicated that a substrate with good surface roughness provides good anchorage of the Ni–P film and hence improved adhesion.

Since the conventional electroless plating is strictly a mass transfer limited process, a number of enhancement techniques such as agitation (Ayturk and Ma, 2009), gas sparging (Altinisik et al., 2005) and sonication (Lu, 2010) are generally employed to facilitate enhanced transportation of reacting species to the surface of the substrate. However, the effect of these mass transfer enhancements on the process performance characteristics has not been quantitatively investigated. In addition, the effect of support surface roughness on these mass transfer coupling phenomena needs to be investigated so as to identify the most competent process. From a surface perspective, since we attempt a pore densification, sequential electroless plating shall progressively target smoother surfaces. An efficient sequential electroless plating process shall attempt smoothening of membrane surface as soon as possible and hence further sequential plating steps shall give rise to higher degree of pore densification. Therefore, ideally the most competent mass transfer enhanced electroless plating process characteristics shall not be influenced with variant surface roughness of the support.

The causal objective of this work is to assess various electroless plating process characteristics so as to simultaneously maximize plating efficiency and pore densification and minimize plating inefficiency and metal film thickness. Such an approach will simultaneously address fabrication of dense metal–ceramic membrane fabrication as well as minimization of metal losses from spent plating solutions. Thereby, the purpose of our experimental investigations is to assess the effect of support surface roughness on all plating characteristics such as efficiency, densification and metal film thickness. Various mass transfer coupling effects studied during electroless plating include solution stirring, membrane stirring and sonication. Since symmetric membrane morphology is considered in this work, near 100% densification of the membrane is not regarded as an important issue. The experimental investigations are attempted to identify the most competent electroless plating process for metal–ceramic composite membrane which can be eventually adopted for engineered support morphologies to fabricate dense membranes. Also in this work, we investigate the plating performance characteristics of nickel plating baths but not palladium plating baths. This is due to the reason that palladium metal is very expensive to carry out rigorous experimentation and nickel being inexpensive could provide good engineering insights which can be experimented for palladium plating baths at a later stage.

In summary, the experimental conditions and parameters in this work are chosen so as to identify the best possible parameters of electroless plating process and its variants. A support with high average pore size (700 nm) is used to screen various combinations of electroless plating process parameters and surface roughness values of the membrane based on evaluated values of conversion, efficiency, film thickness and pore densification.

2. Experimental

2.1. *Preparation of ceramic supports*

Low cost kaolin based disk shaped ceramic supports, were prepared using the raw materials presented in Table 1. Details with respect to the preparation of these ceramic supports were presented in Nandi et al. (2008). These membranes were sintered at a temperature of 1173 K. After sintering process, the membranes achieved hard, rigid and porous texture with an average pore diameter of 700 nm. The membranes also possessed excellent corrosion resistance towards basic media and hence morphological modifications in the support structure were not anticipated during the plating process. Since the as-prepared ceramic membranes are larger in dimension with generally uneven surfaces (Nandi et al., 2008), pre-treatment by means of polishing and cleaning is required before they are suitable for experimentation. Hence, the fabricated membranes were polished using silicon carbide abrasive paper to obtain flat microfiltration membranes with required dimensions (50 mm diameter and 4 mm thickness). Abrasive papers