Ultrasonics Sonochemistry 21 (2014) 1382–1391

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Efficacy of reducing agent and surfactant contacting pattern on the performance characteristics of nickel electroless plating baths coupled with and without ultrasound

Amrita Agarwal, Murali Pujari, Ramgopal Uppaluri *, Anil Verma

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India

ARTICLE INFO

Article history:
Received 23 October 2013
Received in revised form 2 January 2014
Accepted 8 January 2014
Available online 21 January 2014

Keywords:
Sonication
Reducing agent
Densification
Ceramic
Surfactant

ABSTRACT

This article addresses furthering the role of sonication for the optimal fabrication of nickel ceramic composite membranes using electroless plating. Deliberating upon process modifications for surfactant induced electroless plating (SIEP) and combined surfactant and sonication induced electroless plating (SSOEP), this article highlights a novel method of contacting of the reducing agent and surfactant to the conventional electroless nickel plating baths. Rigorous experimental investigations indicated that the combination of ultrasound (in degas mode), surfactant and reducing agent pattern had a profound influence in altering the combinatorial plating characteristics. For comparison purpose, purely surfactant induced nickel ELP baths have also been investigated. These novel insights consolidate newer research horizons for the role of ultrasound to achieve dense metal ceramic composite membranes in a shorter span of total plating time. Surface and physical characterizations were carried out using BET, FTIR, XRD, FESEM and nitrogen permeation experiments. It has been analyzed that the SSOEP baths provided maximum ratio of percent pore densification per unit metal film thickness ($\frac{PPD}{\delta}$) and hold the key for further fine tuning of the associated degrees of freedom. On the other hand SIEP baths provided lower ($\frac{PPD}{\delta}$) ratio but higher PPD. For SSOEP baths with dropwise reducing agent and bulk surfactant, the PPD and metal film thickness values were 73.4% and 8.4 μm which varied to 66.9% and 13.3 μm for dropwise reducing agent and drop surfactant case.

1. Introduction

Electroless nickel deposition occurs due to the accretion of metal particles on a solid substrate. The autocatalytic nickel electroless plating (ELP) process is a relatively slower process, and thus several researchers have conceptualized the need for suitable supplements to enhance the rate of metal deposition on the porous surface without compromising upon the quality of the deposition. Relevant techniques that have been identified include membrane agitation [1], vacuum [2], sonication [3], surfactant [4], hydrothermal [5] and gas sparging [6]. However, from the perspectives of combinatorial plating characteristics, ease of operation and scalability, sonication and surfactant induced ELP are the most promising options that need to be further investigated and examined for their optimality.

During sonication assisted nickel electroless plating, the ultrasonic energy accelerates and improves the chemical reactivity in the solution as well as on the solid–liquid interface. The origin of sonochemical effects is cavitation. Cavitation in a sonicator bath results in mechanical effects by cavity collapse onto the metal/liquid–substrate surface thereby ensuring rapid mass transfer, surface cleaning, particle size reduction, thin film preparation, agglomeration of crystals and metal activation. It facilitates the step wise formation, growth, and subsequent implosive collapse of bubbles in the liquid [7], which thereby influences the metal depositional characteristics. Many researches have inferred that sonication assisted metal deposition enables the synthesis of nano particles and efficient deposition of metals on different substrates [3,7,8]. On the other hand, the addition of a surfactant during ELP influences particle dispersion and metal plating rates and thereby increases the mechanical bonding strength [9].

In the field of metal membrane fabrication, researches have either explored surfactant [4,10–13] or sonication [14,15] rate enhancement techniques separately and their coupled effect during ELP has been investigated for other chemical engineering applications. Recently our research group carried out a comparative assessment of surfactant and sonication induced electroless plating baths [16,17] and inferred that surfactant induced electroless plating (SIEP) baths provide better surface engineering and combinatorial performance characteristics [16] whereas sonication induced electroless plating (SOEP) baths were favorable in terms of enhancing

* Corresponding author. Tel.: + 91 361 2582260; fax: +91 361 2582291.
E-mail address: ramgopalu@iitg.ernet.in (R. Uppaluri).

1350-4177/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ultsonch.2014.01.015

Nomenclature

A_m	permeable area of the membrane, m^2
Q	volumetric flow rate, $\frac{m^3}{s}$
P_2	Membrane pressure at permeate side, pa
ΔP	trans-membrane pressure drop, pa
d_p	average pore size, μm
$\left(\frac{\varepsilon}{q^2}\right)$	effective porosity
J	flux through the membrane, $(\frac{mol}{m^2 s})$
i	hour of nickel plating(as exponent)
$\bar{J}_0$	average flux through the support, $(\frac{mol}{m^2 s})$
$\bar{J}_i$	average flux through the membrane after *i*th hour of nickel plating, $(\frac{mol}{m^2 s})$
C_i	initial concentration of Ni^{+2} in the plating solution, $\frac{mol}{L}$
C_f	average Ni^{+2} solution concentration after plating, $\frac{mol}{L}$
x	conversion
η	plating efficiency, %
w_0	dry weight of the membrane before plating, g
w_i	dry weight of the membrane after *i*th hour of plating, g
w	total amount of nickel originally available in the plating bath, g
n	number of plating cycles
V_0	volume of plating solution in each plating cycle, L
M_{Ni}	molecular weight of nickel metal $\frac{g}{mol}$
ρ_{Ni}	density of nickel metal, $\frac{g}{cm^3}$
$\bar{r}_i$	plating rate, $\frac{mol}{Ls}$
t_i	time of plating for the *i*th hour, hr
PPD	percent pore densification, %
ELP	electroless plating
CEP	conventional electroless plating
SIEP	surfactant induced electroless plating
SOEP	sonication induced electroless plating
CEP–BR	conventional electroless plating – bulk reducing agent
SOEP-BR	sonication induced electroless plating – bulk reducing agent
SIEP-BR-BS	surfactant induced electroless plating – bulk reducing agent-bulk surfactant
SIEP-DWR-BS	surfactant induced electroless plating–dropwise reducing agent-bulk surfactant
SSOEP-DWR-BS	coupled sonication and surfactant induced electroless plating–dropwise reducing agent-bulk surfactant
SIEP-DWR-DWS	surfactant induced electroless plating–dropwise reducing agent-dropwise surfactant
SSOEP-DWR-DWS	coupled sonication and surfactant induced electroless plating–dropwise reducing agent-dropwise surfactant

plating rates. Despite improving the plating rates, the SOEP baths failed to achieve higher pore densification and have phenomenally contributed to the layering effect without improving upon the pore coverage and densification. Since SIEP process also has fundamental limitations in terms of limited enhancement in the plating rate, a further enhancement in the plating rate without jeopardizing upon the pore densification was desired. To achieve the same, it was hypothesized that a combination of sonication and surfactant would suffice the purpose of targeting the fabrication of dense metal composite membranes.

Further, few researchers [3,18,19] have investigated ELP coupled with sonication and surfactant variants for the development of products other than metal ceramic membranes. But till date, the literature is scarce on the coupled effect of two most scalable rate enhancement techniques namely surfactant and sonication for the fabrication of metal ceramic composite fabrication using ELP technique.

On the other hand, surfactant induced electroless plating (SIEP) and combined surfactant and sonication induced electroless plating (SSOEP) baths can be operated in several ways. As a first alternative, all the constituents can be mixed initially and plating could be initiated. Otherwise, the reducing agent can be added in a phase wise or continuous mode to the mixture of surfactant and metal solution in an ELP bath. As a third alternate, both reducing agent and surfactant can be added in a phase wise and continuous mode to the ELP baths. While these options may appear naïve for the general application of ELP, they may be of paramount relevance for dense metal composite membranes. Till date there is no literature that elaborates upon the role of contacting pattern of the surfactant in electroless plating bath for dense composite membrane fabrication. All relevant literatures [10,11,20] addressed bulk addition of surfactant for metal deposition using electroless plating. The bulk addition of surfactant encourages adsorption of surfactant on the membrane surface which promotes uneven charge distributions on the surface [4] .This encourages greater metal nucleation in the solution. Variation in the surfactant contacting pattern is hypothesized to promote better depositional characteristics and membrane pore densification due to lesser adsorption of surfactants on the substrate surface. Thus to increase the efficacy of the electroless plating process, there is a need to focus upon the contacting pattern of the dispersing agent (surfactant).

Also, a reducing agent such as hydrazine hydrate is highly heat sensitive and maintaining a steady concentration of the same is highly cumbersome [21]. Conceptually, to overcome the same, a highly controlled reducing agent addition strategy has to be adopted in this work. Such an addition of reducing agent to an electroless plating process would be similar to the optimal current density utilization in an electroplating process. The adopted strategy for controlled addition of the reducing agent in this work corresponds to the dropwise addition of the reducing agent during the SIEP/SSOEP process.

This work addresses various types of SIEP and SSOEP processes considering options such as bulk addition of surfactant (BS), continuous (dropwise) addition of surfactant (DWS) and continuous (dropwise) addition of reducing agent (DWR). This work addresses two major objectives. Firstly, it elaborates upon the comparative assessment of SIEP and SSOEP processes supplemented with the dropwise addition of the reducing agent. Secondly, it focusses upon the dropwise addition of the dispersing agent (surfactant) for SIEP and SSOEP baths. The ultimate goal of our experimental investigations is to identify the best process that can provide maximum percent pore densification (PPD), plating rate ($\bar{r}_i$), plating efficiency (η) and minimum metal film thickness (δ).

2. Experimental

Low cost circular disk shaped ceramic supports with an average pore size of 200–250 nm were prepared using the raw materials presented in Table 1. The laboratory fabricated circular ceramic substrates possessed a diameter of 36 mm and a thickness of 3.5 mm. The fabrication methodology consists of the following hierarchical steps: mixing of raw materials; casting of the mixture into circular moulds; drying of the raw discs at 100 °C; sintering at 900 °C with a controlled heating/cooling rate (1.5 °C/min); polishing of the membranes and finally ultrasonically cleaning the