Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 253 (2006) 2189–2195
applied surface science
www.elsevier.com/locate/apsusc

ZrO_2-reinforced Ni–P plate: An effective catalytic surface for hydrogen evolution

S.M.A. Shibli *, V.S. Dilimon, T. Deepthi

Department of Chemistry, University of Kerala, Kariavattom Campus, Trivandrum 695 581, Kerala, India

Received 20 January 2006; received in revised form 7 April 2006; accepted 7 April 2006
Available online 24 May 2006

Abstract

Nickel and its alloys have recently been emerged as potential catalytic electrode materials for hydrogen evolution reaction in alkaline media. The present work contemplates reinforcement of electroless Ni–P plate with ZrO_2. The plate showed very high stability and excellent electrocatalytic activity. In situ incorporation of ZrO_2 resulted in increase in the rate of deposition of Ni on steel substrate. There was high activation during the initial stage of the plating also. The electrocatalytic activity of the ZrO_2-reinforced Ni electroless plate was found to be highly reproducible and long lasting when used for hydrogen evolution reaction.

Keywords: Nickel electrode; Hydrogen production; Electrocatalysis; Electroless nickel plating; Zirconium oxide-reinforcement

1. Introduction

Nickel and nickel alloy plates are good catalytic electrode materials for hydrogen evolution reaction [1–5]. Though Ni has resistance to corrosion in alkaline environments, it slowly loses its electrocatalytic activity with time when used for hydrogen evolution reaction [6]. Electroless Ni–P plates have many superior properties than electrodeposited Ni. Because of the phosphorus content, electroless Ni–P plate is harder and has higher corrosion resistance [7]. Electroless Ni–P plates reinforced with composites also possess unique properties of conventional electroless Ni–P plates such as uniformity of deposition, high hardness and good corrosion resistance. The stability of Ni–P plating can be improved considerably by reinforcing with hard composites such as TiO_2, Al_2O_3, etc. [8,9]. Reinforcing of Ni–P plating with other stable electrocatalytic composites further improves the electrocatalytic performance [10–14]. An electrocatalytic synergistic effect is cause for the improvement in the activity of such plate.

Zirconium dioxide is a good catalytic composite for reinforcing Ni plating [15–17]. The desirable influence of ZrO_2 composite on improving the electrocatalytic activity of electroplated Ni on copper substrate has been reported elsewhere [15]. In the present study, electroless Ni–P–ZrO_2 composite plating on steel substrate was explored and investigated in view of achieving high plating stability and good electrocatalytic activity for hydrogen evolution reaction in NaOH medium. ZrO_2 composite was found to incorporate into the plate uniformly yielding high stability and good electrocatalytic activity for hydrogen evolution. The results are discussed in this paper.

2. Experimental procedures

2.1. Electroless plating

Mild steel coupons having the composition – carbon: 0.09%, manganese: 0.034%, phosphorus: 0.036%, silicon: 0.0487% and aluminum: 0.029% – were used as the substrate for the plating. The dimension of the mild steel coupons was 5 cm × 5 cm × 0.2 cm. The surface was polished with different grades of fine emery papers up to 1000 grade and washed with distilled water. The coupons were treated with 5% NaOH for 5 min and then treated with 3% HCl for 5 min. The coupons were sensitized in a solution containing 10 g/L $SnCl_2$ in 40 mL/L HCl (37%). After sensitization the surface was activated in a solution of 1 g/L $PdCl_2$ in 10 mL/L HCl (37%).

* Corresponding author. Tel.: +91 471 2167230; fax: +91 924 9863611.
E-mail address: smashibli@yahoo.com (S.M.A. Shibli).

0169-4332/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2006.04.025

The composition of the electroless bath was—nickel sulphate: 30 g/L, succinic acid: 25 g/L and sodium hypophosphite: 25 g/L. The bath pH was adjusted to 4.5 by adding ammonia solution. The required amounts of ZrO_2 were also added into the bath during the making of Ni–P–ZrO_2 composite plates. The plating temperature was kept at 85 ± 2 °C. The bath was stirred continuously by using a magnetic stirrer during the plating process. The duration of plating was 2 h. The variation in the deposition rate of Ni–ZrO_2 composite plate on the steel substrate as a function of the amount of ZrO_2 in the bath was determined by weighing coupons before and after electroless deposition. The potential variation of the coupons in the plating bath, during the plating process, was monitored with respect to SCE as a function of time. The plating bath was connected to another beaker containing KCl solution by means of a salt bridge so as to prevent the intermixing of bath solution with KCl solution in SCE. The potential values were then measured with respect to SCE placed in KCl solution.

2.2. Physico-chemical characterization

Physical characteristics of the plates such as hardness, thickness, adherence and porosity were determined as per standard methods. The hardness of the plates was determined by using Vickers microhardness indenter (ASTM E E 364-99) with a 100 gf load applied for 25 s. The adhesion of the plates was evaluated by bend test (ASTM B 571-91). Thickness of the plates was determined as per ASTM B 499-88. The porosity of the plates was characterized by using ferroxyl reagent test. A solution of potassium ferricyanide, sodium chloride and agar–agar in hot water was used as the ferroxyl reagent. The plates were etched in 5% HCl solution for 5 min. The etched plates were washed with distilled water, dried and the morphology was studied by using SEM. The chemical composition of the plates was analyzed by using EDAX attached to the SEM instrument.

2.3. Electrochemical characterization

The electrochemical behavior of the plating was studied by using ac impedance spectroscopic analysis in 32% NaOH electrolyte. The analysis was carried out at the open circuit potential of the electrode. An impedance spectrometer of AUTOLAB PGSTAT 30 with a FRA2 software of FRA version 4.9 was used. The analysis was carried out in the frequency range from 1 MHz to 10 Hz. An Ag/AgCl/KCl was the reference electrode and a platinum mesh was the counter electrode. Cathodic and anodic polarization behavior of the electrodes in 32% NaOH solution was studied galvanostatically. A platinum grid was used as the counter electrode and an Hg/HgO/1N OH^- electrode with Luggin capillary was used as the reference electrode.

3. Results and discussion

3.1. The physico-chemical characteristics

The stability in alkaline medium is one of the major requirements of an electrode material during hydrogen evolution in alkaline electrolyte. Electrocatalytic nickel plating of uniform surface with high hardness and corrosion resistance would be the best choice for large scale hydrogen production. The chemical composition of the plates could also strongly influence its stability. In electroless Ni–P plating, the variation in phosphorus content significantly influences the crystal structure of the deposit and hence its characteristic properties like corrosion resistance, wear and abrasion resistance, etc. [18,19]. The nature of composite and its concentration could also influence further if the plating was reinforced [8,9]. The physico-chemical characteristics of the present electroless Ni–P plates reinforced with different amounts of ZrO_2 are compared in Table 1. The physical properties such as hardness, adherence and wear resistance were considerably improved by means of ZrO_2 incorporation. Thickness and porosity of the plating were not considerably influenced by means of ZrO_2 reinforcement.

The Zr content in the plates was found to be increased proportionally with increase in ZrO_2 content in the bath up to ~9 g/L (Table 1). There was no considerable change in the Zr content in the plates when the ZrO_2 content in the bath was increased further above 9 g/L. The observed improvement in the physical properties due to change in ZrO_2 content was also found to be ceased above this concentration. It was the variation in ZrO_2 content in the plates that was responsible for the variation in the physical properties. The variation in phosphorus content could have influenced the physical properties but it was almost same in all the plating (~9%). Thus an optimum content of ZrO_2 in the plate was obtained by fixing ZrO_2 content in the

Table 1
Physico-chemical characteristics of the Ni–P electroless plates with and without ZrO_2 reinforcement

ZrO_2 content in the bath (g/L)	Composition of fresh coatings		Composition of coatings after hydrogen evolution		Physical properties of the coatings		
	P (%)	Zr (%)	P (%)	Zr (%)	Hardness (HVN)	Thickness (μm)	Wear resistance
0	9.1	0	8.9	0	430	10–12	Fair
3	9.3	2.1	9.2	2	515	12–14	Good
6	9.7	4.3	9.2	4.2	553	13–16	Good
9	8.9	6.8	9	6.9	590	13–16	Better
12	9.2	7.2	8.8	7	592	14–15	Better
15	9.8	6.9	9.7	6.9	597	14–16	Better