Simultaneous reduction of perrhenate and nickel ions by hypophosphite

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1. Introduction

Electroless deposition of Ni–P alloys with Co, W, Mn, Re, etc. allows metal layers to be formed with some unique magnetic properties suitable for vertical recording [1]. Ni–P–Re coating formation by electroless plating with a high (up to 40 mass %) rhenium content from perrhenate containing solution has been reported [2]. An unusually high efficiency of hypophosphite used in the overall process was found [3]: the amount of hypophosphite required for reducing nickel, perrhenate and hypophosphite ions to Ni, Re and P was found to be even lower than that calculated, assuming hypophosphite as a one-electron reducing agent as usual [4].
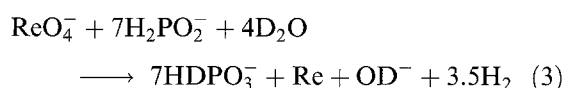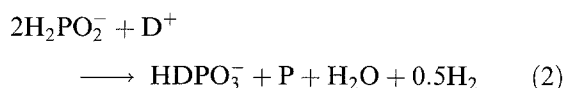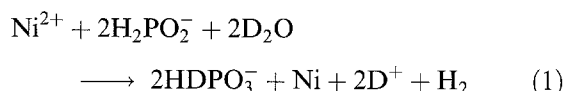
However, it is difficult to investigate such complex systems as simultaneous reduction of several metal ions by hypophosphite, because hypophosphite itself is used in several reduction reactions in parallel to its catalytic oxidation by water. Therefore, the mechanism of catalytic oxidation of hypophosphite on nickel [5] and Ni(II) reduction by hypophosphite [6] was studied previously using electrochemical mass spectrometry [7]. The stoichiometry of phosphorus formation reaction in electroless Ni–P plating was also studied [8] by deuterium labelling to evaluate hypophosphite reaction with water.

Perrhenate ion reduction in the course of electroless Ni–P–Re plating was studied in the present work.

2. Experimental details

The solution for electroless deposition of Ni–P–Re coatings contained (mol dm^{-3}): NiCl$_2$ − 0.1; NaH$_2$-PO$_2$ − 0.12; KReO$_4$ − 0−0.025; NH$_2$CH$_2$COOH − 0.4 at pH 8 and temperature 90° C. Water-free salts, deuterated glycine ND$_2$CD$_2$COOD (deuterium content 96 mol %) and D$_2$O (deuterium content 99.8 mol %) were used to prepare the solution for the deuterium tracer experiments. The gas evolved was collected and analysed using a mass spectrometer MI-1201 (experimental details are given elsewhere [6]). Usual techniques were used for other analyses including titrimetric detection of hypophosphite with vanadate, nickel deposited − complexonometrically with EDTA, both phosphorus and rhenium − colorimetrically with molybdate and thiourea respectively. The amount of hypophosphite used was calculated according to the

following reactions [1–4]:

$$Ni^{2+} + 2H_2PO_2^- + 2D_2O$$
$$\longrightarrow 2HDPO_3^- + Ni + 2D^+ + H_2 \quad (1)$$

$$2H_2PO_2^- + D^+$$
$$\longrightarrow HDPO_3^- + P + H_2O + 0.5H_2 \quad (2)$$

$$ReO_4^- + 7H_2PO_2^- + 4D_2O$$
$$\longrightarrow 7HDPO_3^- + Re + OD^- + 3.5H_2 \quad (3)$$

$$H_2PO_2^- + D_2O \longrightarrow HDPO_3^- + HD \quad (4)$$

CVs were recorded using a programming potentiostat PI-50-1 (Russia) with a potential scan rate of 10 mV s^{-1}; potentials are given with respect to the SHE. The X-ray photoelectron spectra were recorded on a VG Scientific spectrometer Escalab MK II (UK).

3. Results and discussion

The voltammetric response of the Ni–P–Re electrode in the electroless nickel plating solution containing perrhenate ion demonstrates a more positive value of the open circuit potential (o.c.p.) and a lower anodic current density in comparison with the Ni–P electrode in the perrhenate-free solution (Fig. 1). This may be explained assuming that the o.c.p. is mixed and taking into account that rhenium does not catalyse anodic hypophosphite oxidation.

A good efficiency of hypophosphite used in Ni–P–Re alloy deposition [3] may be due to the following reasons: (i) reaction of hypophosphite with water (Reaction 4) does not proceed in the presence of a perrhenate ion (a new electron acceptor); (ii) the perrhenate ion is reduced to metal rhenium and/or to lower oxides; (iii) the second electron of hypophosphite is used for the reduction of the perrhenate ion (the possibility of Ni(II) ions reduction by two-electron oxidation of hypophosphite in alkaline solutions is discussed elsewhere [9]).

(i) Deuterium labelling allows the amount of hypophosphite used in the reaction with water to be found when comparing isotopic composition of the gas evolved with analyses of the hypophosphite used in the overall process and the amount of Ni, P and Re deposited (Reactions 1–4). Reaction of hypophosphite with water can be evaluated by the mass spectrometric analysis of the gas evolved, since only Reaction 4 leads to formation of gas containing equal amounts of hydrogen and deuterium.
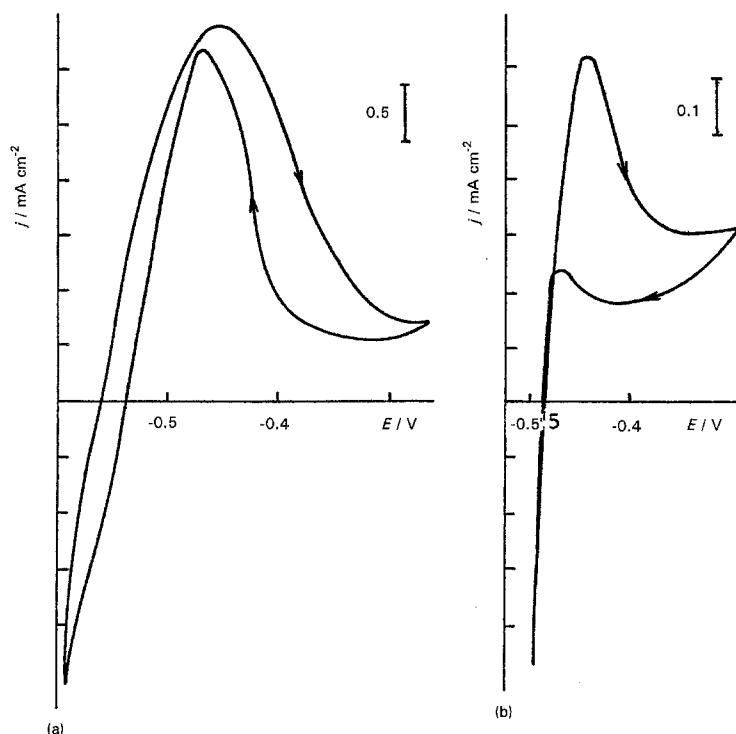
Fig. 1. CV of the Ni–P (a) and Ni–P–Re (b) electrodes. The solution contained (mol dm^{-3}): NiCl$_2$ – 0.1; NaH$_2$PO$_2$ – 0.12; KReO$_4$ – 0.0 (a) or 0.017 (b); NH$_2$CH$_2$COOH – 0.4 at pH 8 and T = 90 °C.

Mass spectrometric analysis of hydrogen evolved in Ni–P–Re alloy deposition using D$_2$O as a solvent shows a deuterium content of ∼ 10 mol % (Table 1). Analyses of the deuterium content in the fractions of the evolved gas (exp. 6 of Table 1) suggest neither hypophosphite hydrogen exchange with D$_2$O in the solution nor hydrogen gas evolved with D$_2$O vapour to proceed to a significant extent under experimental conditions. The value of the deuterium content in the gas evolved is nearly the same as that in the absence of perrhenate [8]. In contrast, the data of analyses of the total hypophosphite used and Ni, P and Re content in the deposit suggest all hypophosphite to be used in Reactions 1–4 (Table 1). This should result, however, in hydrogen evolution from the P–H bond of hypophosphite alone, as opposed to the data of mass spectrometric analysis; reaction of hypophosphite with water occurs almost to the same proportion in both perrhenate-containing and perrhenate-free solutions. This implies that less than seven electrons are used per single perrhenate ion reduction, that is, the latter could be expected to

be reduced only to lower oxides. The deuterium content in the gas evolved calculated from the data of Table 1 taking different equations of perrhenate reduction gives the best fit with the experimental value assuming five electrons per one perrhenate molecule are used.

(ii) The composition of electrolessly deposited Ni–P–Re alloys was examined by X-ray photoelectron spectroscopy (XPS) to determine the rhenium oxidation state. The specific doublet of Re $(4f_{7/2})$ and Re $(4f_{5/2})$ levels with the binding energies (E_b) of 40.1 and 42.5 eV, respectively, was found (Fig. 2). Oxygen-containing species $(E_b$ ∼ 45.0 eV) and a trace amount of KReO$_4$ $(E_b$ ∼ 46.0eV) [10] were determined only on the surface of the Ni–P–Re coating: they both disappear after Ar$^+$ sputtering of the specimen down to 5 and 20 nm depth.

The peak with E_b = 856.2 eV close to the main peak of metal nickel at E_b = 852.5 eV of Ni $(2p)$ level may be attributed to Ni(OH)$_2$ species [11] at the surface of the coating (Fig. 3). Ar$^+$ sputtering to 5 and 20 nm leads to the pure nickel spectrum (Fig. 3),

Table 1. Amount of nickel, rhenium and phosphorus deposited, and hypophosphite used in the overall process and in Reactions 1–4 in μmol (n.d. – not determined), and deuterium content in the gas evolved (fractions every 30 min. in exp. 6)

Exp.	Experimental data					H$_2$PO$_2^-$ calc., used in reactions			
	Ni	Re	P	$\Delta H_2 PO_2^-$	D$_2$/mol%	(1)	(2)	(3)	(4)
1	305	99	16	n.d.	9.2	610	32	693	n.d.
2	297	99	14	1255	11.8	594	28	693	−60
3	250	89	16	n.d.	10.8	500	32	623	n.d.
4	265	83	14	1140	10.4	530	28	581	1
5	285	97	16	1260	11.9	570	32	679	−21
6	340	124	22	1550	10.3; 9.5; 9.6	680	44	866	−42

The solution contained (mol dm^{-3}): NiCl$_2$ – 0.1; NaH$_2$PO$_2$ – 0.12; KReO$_4$ – 0.017; ND$_2$CD$_2$COOD – 0.4; pH 8; T 90 °C; solvent: D$_2$O.
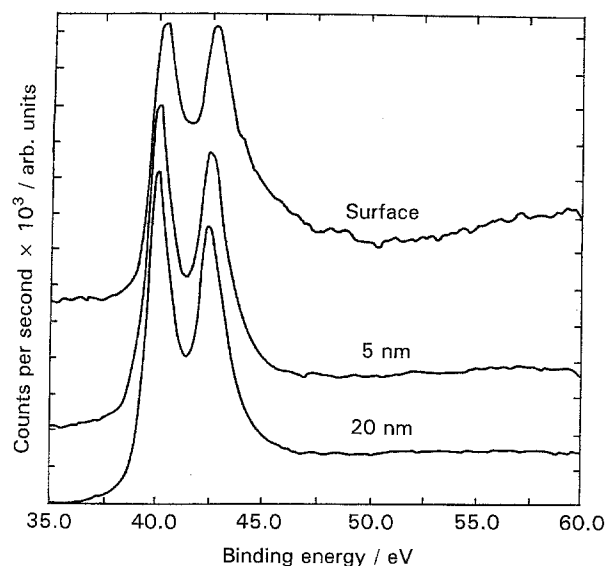
Fig. 2. XPS data for the Re ($4f$) spectra of the electrolessly deposited Ni–P–Re alloy.

that is, inner layers of the coating are free of oxidized nickel species.

Two peaks of P ($2p$) level in the XPS spectra with E_b of 129.8 and 132.9 eV correspond to free phosphorus and phosphite or phosphate ion [11]; the second peak diminishes with Ar^+ sputtering so that the first one prevails in deeper layers. An appreciable amount of oxygen is present at the surface of the Ni–P–Re alloy, however, it is negligible after Ar^+ sputtering up to 20 nm.

Therefore, metal rhenium and nickel, as well as elemental phosphorus, are concluded to be the main components of the electrolessly deposited Ni–P–Re alloy. It should be noted, that rhenium oxides are not present in the coating according to XPS data.

(iii) Alternatively, the second electron of hypophosphite may be assumed to take part in perrhenate reduction: for example, hypophosphite is known as a two-electron reducing agent in homogeneous reduction of perruthenate to ruthenate [12]. Similarly, perrhenate could be assumed to be reduced homogeneously to rhenate ion by two-electron reduction at the first step and then to metal rhenium in a heterogeneous one-electron reduction step. Such a sequence of reactions leads to rhenate formation in the solution. However, UV absorption spectra did not show any change in the absorption bands after heating the solution. Therefore, heterogeneous two-electron oxidation of hypophosphite seems to proceed to some extent in the course of perrhenate ion reduction to rhenium. Some intermediate formed in hypophosphite anodic oxidation may take part in perrhenate reduction (phosphite formed as a result of anodic hypophosphite oxidation was found to be unable to reduce perrhenate). Possibly, atomic hydrogen, formed in the hypophosphite anodic oxidation reaction at the catalyst surface according to [4], takes part to some extent in the reduction of perrhenate ion to rhenium metal.
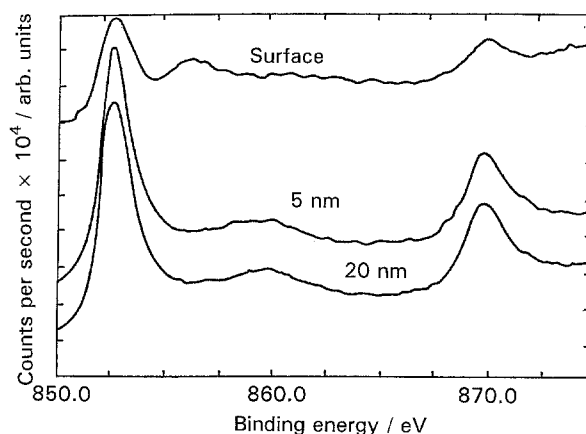

Fig. 3. XPS data for the Ni ($2p$) spectra of the electrolessly deposited Ni–P–Re alloy.

4. Conclusions

Reduction of water by hypophosphite during Ni–P–Re alloy deposition proceeds in nearly the same proportion as that in the case of Ni–P deposition according to the mass spectrometric analysis of the gas evolved in deuterium-labelled electroless plating solutions. Perrhenate ion is reduced to metal rhenium as shown by the XPS analysis of the electrolessly deposited Ni–P–Re coating. Atomic hydrogen is expected to take part in perrhenate reduction at the catalyst surface resulting in a high hypophosphite efficiency in the overall electroless Ni–P–Re deposition process.

Acknowledgements

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