Electro catalytic amorphous nickel alloy

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Nickel and nickel based alloy deposits are used as cathode materials for hydrogen evolution. Watt's bath modified with thiourea was used to deposit Ni-S and Ni-S-Co alloys. In presence of thiourea, Watt's bath offered amorphous Ni-S alloy. In presence of $CoCl_2$ and thiourea, amorphous Ni-S-Co alloy was formed. Hydrogen evolution reaction occurred faster on amorphous Ni-S-Co alloy compared to amorphous Ni-S alloy from 28 wt% NaOH. Hydrogen evolution reaction rate increased with temperature on these amorphous alloys. A fast Volmer followed by slow Heyrovsky reaction occurred on the surfaces of these alloys. Heat treatment of amorphous Ni-S-Co alloy decreased the electro catalytic activity due to the disturbance in the amorphous structure.

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Hydrogen is an ideal eco-friendly source of energy. In order to use it as the regular source of energy many new methods are created among which water electrolysis is one. Nickel and nickel based alloys are chosen as cathode materials. Nickel sulphide containing molybdate[1] was used as a cathode. Nickel-S alloy was deposited from nickel ammonium sulphate bath. When sodium thiosulphate was added to the bath, 13% sulphur in the deposit was obtained[2]. Thiourea was also used as a source of sulphur[3]. Thiourea was also employed to get 10 to 20 wt% sulphur in the Ni-S alloy deposit[4,5]. The enhanced electrochemical activity on these alloy was due to adsorbed hydrogen.

The present paper deals with the deposition of amorphous Ni-S and Ni-S-Co alloys from modified Watt's bath and evaluation of their catalytic activity for hydrogen evolution reaction.

Experimental Procedure

Electro deposition was carried out on a mild steel substrate. The substrates (5 × 2 × 0.025 cm) were polished with fine grid paper and degreased with trichloroethylene. They were electro cleaned cathodically for 2 min in an alkaline solution composed of 35 gpl NaOH, 25 gpl Na_2CO_3 and 10 gpl trisodium phosphate at 343 K with a current density of 3 A/dm². They were washed in running water and dipped for 5 s in 5% H_2SO_4 solution. Finally thorough washing and drying were done.

Nickel sulphur electrodeposits were obtained from a modified Watt's bath of 200 gpl $NiSO_4.7H_2O$, 40 gpl $NiCl_2.6H_2O$, 35 gpl boric acid and 100 gpl thiourea. The pH of the bath (4.3-4.7) was maintained and monitored by digital pH meter. Nickel sulphur cobalt electrodeposits were also deposited from the above bath with various concentrations of $CoCl_2$ (10-30) gpl. Cathode potentials during electro deposition was monitored using a Saturated Calomel Electrode. The alloy surfaces deposited on copper substrates were characterized by JEOL X-ray diffraction unit and at selected points on the surface, cobalt and sulphur concentrations were determined by EPMA.

Hydrogen evolution reaction was studied in 28 wt% NaOH solutions. The electrochemical experiments were studied using a PARC model 173 potentiostat/galvanostat. One cm² area of the Ni-S and Ni-S-Co alloy deposits were used as working electrodes. An $Hg/HgO/OH^-$ electrode was used as a reference along with a large platinum foil as auxiliary electrodes. To minimize IR drop, a Luggin capillary was used. A pre electrolysed 28wt% NaOH solution was used.

Results

Electro deposition

Ni-S alloy electro deposition on mild steel was carried out from modified Watt's bath. Current density increased the % sulphur content in the alloy (Table 1). When the alloy deposition current density was 10 mA/cm², weakly crystallized Ni_3S_2 was seen on the Ni-S alloy. While at 30 mA/cm², some weak peaks corresponding to nickel appeared. At an

Table 3 — Parameters obtained for hydrogen evolution reaction on amorphous Ni-S alloy

Temperature K	Tafel slopes Low η	mV/decade High η	Exchange current density Low η	mA/cm^2 High η
308	92	143	2.9	15.3
322	81	140	3.5	19
338	69	139	4.2	30
353	64	133	5.6	44

Table 4 — Parameters obtained for hydrogen evolution reaction on amorphous Ni-S-Co alloy

Temperature K	Tafel slopes Low η	mV/decade High η	Exchange current density Low η	mA/cm^2 High η
308	94	155	3.2	17.5
322	93	149	3.9	22.8
338	82	139	4.8	32
353	62	121	6.2	51
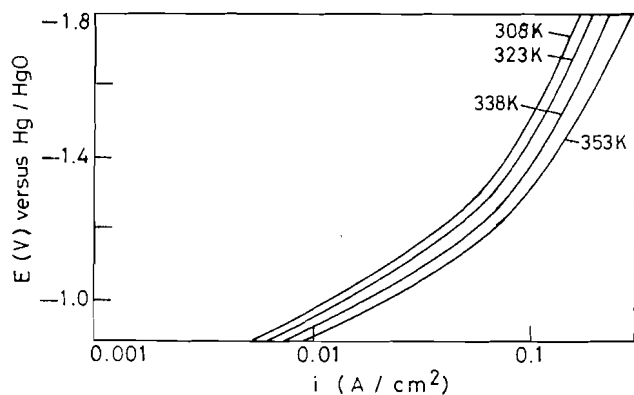
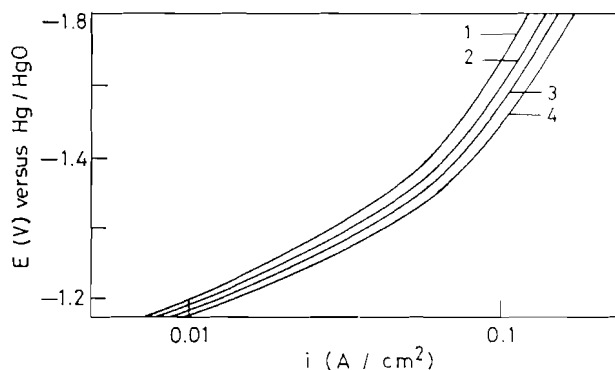Fig. 5 — Steady state polarization curves for amorphous Ni-S-Co alloy at various temperatures

Fig. 6 — Tafel polarization curves for amorphous Ni-S-Co electrodeposits in various pHs (1) 13.6, (2) 12.5, (3) 11.8, (4) 10.8

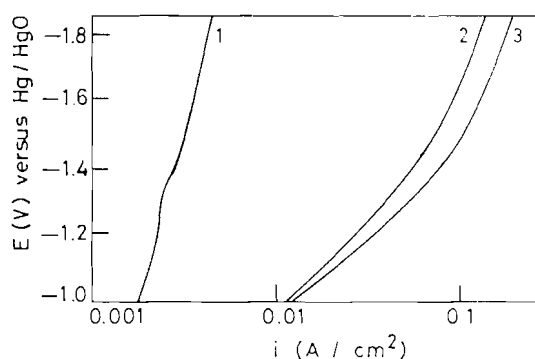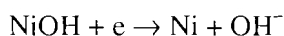Ni-S and Ni-S-Co alloy deposits in NaOH solutions (pH 12). In the lower and higher over potentials regions, the exchange current densities on Ni-S-Co> Ni-S> mild steel. In the higher over potential region value of 1.7, 39.2 and 50.1 mA/cm^2 were obtained on mild steel, Ni-S alloy and Ni-S-Co alloy respectively.

Heat treatment

Amorphous Ni-S-Co alloy deposits were heat treated and DTA curves obtained on the alloy revealed two peaks at 371 and 445K respectively suggesting two phase transformations. The amorphous nickel transformed to crystalline nickel. During the second peak region Ni$_3$S$_2$ crystals were seen. XRD patterns obtained at 353 K alloy deposit revealed only amorphous Ni-S-Co alloy (Fig. 8). On 413 K heat treated alloy deposit some Ni$_{3-x}$ S$_2$ phase was seen. Hydrogen evolution reaction was studied on heat treated alloy. Hydrogen evolution reaction was found to occur faster on amorphous alloy than on heat treated alloy deposits. Heat treatment temperatures favoured crystallinity and thus decreased the h.e.r rate (Table 5).

Discussions

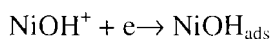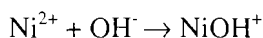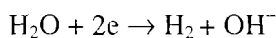From uncomplexing solutions the deposition of nickel in the acidic pH range was found to occur[6] as:

Fig. 7 — Polarization curves for mild steel amorphous Ni-Sand amorphous Ni-S-Co alloy deposits at 353K in NaOH solutions (pH 13.6) (1) Mild steel, (2) amorphous Ni-S, (3) amorphous Ni-S-Co alloy

$$H_2O + 2e \rightarrow H_2 + OH^-$$

$$Ni^{2+} + OH^- \rightarrow NiOH^+$$

$$NiOH^+ + e \rightarrow NiOH_{ads}$$

$$NiOH + e \rightarrow Ni + OH^-$$

In presence of ethylamine[7], a complexant, nickel deposition was found to occur as:

$$Ni(II) \text{ complex} + 2OH^- + 2e \rightarrow Ni + 2OH^- + (\text{amine})$$
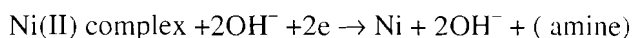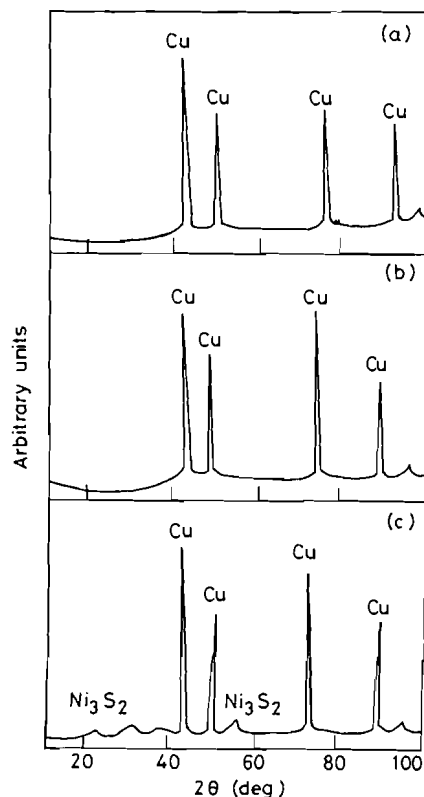
Fig. 8 — XRD patterns of Ni-S-Co alloy deposits heat treated for one hour at various temperatures

Table 5 — Effect of heat treatment on the hydrogen evolution reaction on amorphous Ni-S-Co alloy at 353 K

Alloy	Tafel slopes Low η	mV/decade High η	Exchange current density Low η	mA/cm^2 High η
Amorphous	62	121	6.2	51
353K	87	137	5.4	46.8
413K	86	145	4.3	35.2
473K	91	159	3.4	28.4

In the present study thiourea forms complexes with nickel and reduction of $Ni\{CS_2(NH_2)_2\}^{2+}$ takes place at negative potentials with the incorporation of elemental sulphur.

$$Ni\{CS_2(NH_2)_2\}^{2+}+2e \rightarrow Ni + (complexant)$$
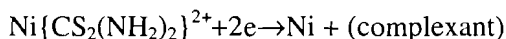
When $CoCl_2$ was added to the bath, there existed $Co\{CS_2(NH_2)_2\}^{2+}$ and $Co\{CS_2(NH_2)_2\}^{2+}$ complexes. Reduction of these complexes gave rise to the deposition of cobalt. Deposition over extended cathodic current densities favoured sulphur content in the alloy. During Ni-S-Co alloy deposition two cathodic reactions are involved. The first one is the

direct depositions of Ni $^{2+}$ and Co^{2+} ions with thiourea, respectively which competes with the first reaction. The cathodic polarization of such complex ions increase with the current density and therefore the contents of nickel and cobalt increase as the deposition of nickel and cobalt ions became predominant. The amorphous structure decreased with increase in cathodic current density. Impedance spectral analysis[8] of hydrogen evolution reaction from 0.5 M H_2SO_4 on deposited ruthenium and rhodium electrodes revealed electron transfer, formation of adsorbed hydrogen and H_2 desorption steps. Rhodium was found to be more electrocatalytic.

In order to correlate M-H bond energy and exchange current density, various ideas like "Volcano" shaped curves were suggested[9,10]. As h.e.r involves the transfer of the electron from an electrode surface (work function), the density of states of electrons close to the energy level of metal surface (density of states at E_F) is an important parameter governing electrochemical reaction rates. The electron density of states at E_F may be increased by forming substitution alloys and inter metallic phases to improve the catalytic activity. In the present study the lattice parameter and inter atomic distances of Ni-Co-S alloyed materials change due to the changes in the arrangement of atoms. When inter metallic bonding results in the reduced lattice parameter, the inter atomic distance increased the density of states at E_F. The amorphous structure of Ni-S-Co alloy offered enhanced catalytic activity due to increased surface area. Heat treatment of the alloys at 413 and 473 K destroyed the amorphous nature and crystallinity did not favour catalytic activity. The catalytic activity became 50% when the heat treatment temperature was 473 K.

Conclusions

(i) In presence of thiourea Watt's bath offered amorphous Ni-S alloy. In presence of $CoCl_2$ and thiourea amorphous Ni-S-Co alloy was formed.

(ii) Hydrogen evolution reaction occurred faster from 28 wt% NaOH on amorphous Ni-S-Co alloy compared to amorphous Ni-S alloy.

(iii) Hydrogen evolution reaction rate increased with temperature on these amorphous alloys.

(iv) A fast Volmer followed by slow Heyrovsky reaction occurred on the surfaces of these alloys.

(v) Heat treatment of amorphous Ni-S-Co alloy decreased the electro catalytic activity due to the disturbance in the amorphous structure.

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