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Effect of triethylamine/anhydrous HF ratio on the anodic polarisation of nickel in acetonitrile media

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Abstract

The effect of the addition of 0.5 M, 1.5 M, 3 M and 4.5 M triethylamine in acetonitrile containing 3 M anhydrous HF (AHF) on the anodic polarisation behaviour of Ni was investigated using cyclic voltammetry and chronoamperometry. The structure and composition of the film formed on a nickel electrode in these media was investigated using SEM and XRD. The severe dissolution noticed in aqueous HF solution decreases significantly in acetonitrile containing AHF. Addition of small molar ratios of triethylamine leads to enhanced uniform dissolution due to the simultaneous presence of H^+ as well as fluoride ions. Further addition of triethylamine suppresses the HF concentration. This leads to anodic dissolution at a significantly more positive potential. Dissolution and film growth occurs in the form of individual crystallites. In all cases, $NiF_2 \cdot 4H_2O$ and another phase is formed on the electrode surface.

Keywords: Anodic polarisation; Nickel; Acetonitrile media; X-ray diffraction; Triethylamine/HF ratio

1. Introduction

In an earlier report on the anodic polarisation behaviour of Ni in acetonitrile–HF and acetonitrile–HF–H_2O systems from this laboratory, some preliminary studies relating to the effect of triethylamine (2 M) addition in CH_3CN–3 M AHF solutions were reported. The significant difference in the cyclic voltammetric (CV) responses between CH_3CN–HF and CH_3CN–HF–triethylamine systems was speculated to be due to the difference in the medium acidity. This aspect was not considered in further detail [1].

In this work, the effect of the addition of various molar ratios of triethylamine and AHF on the voltammetric response as well as current–time curves under potentiostatic polarisation conditions is reported. In addition, SEM and XRD studies were also carried out to further establish the characteristics of the film formed on the Ni electrode surface.

2. Experimental details

Freshly distilled AR grade acetonitrile (CH_3CN) and standardised 20.0 M aqueous HF solutions were used for the preparation of acetonitrile/water mixtures. Preparation of 2.0 M and 5.0 M AHF in acetonitrile medium required the addition of a quantity of AHF (containing <1 ppm water; TANFAC, India) to acetonitrile under low-temperature conditions, due care being taken to avoid moisture absorption. The content of HF, which was always taken in slight excess during AHF transfer, was later determined and standardised by adding the required quantity of solvent. Acetonitrile–AHF–triethylamine solutions were also prepared by this method [2].

The Ni working electrode was polished to a mirror finish and washed well with triply distilled water and then with trichloroethylene before use. Since an insoluble passive NiF_2 film is formed on the Ni electrode during each potential cycle, the electrode had to be repeatedly cleaned and polished after each CV experiment in order to obtain reproducible results.

Other experimental details include the use of a Pt foil counter electrode, Pd/H_2 reference electrode, an all-polypropylene cell assembly and FEP tubing to avoid HF/glass contact. The experiments were carried out at 303 ± 1 K [1,2]. For obtaining scanning electron micrographs, a JEOL, model 30CF instrument was used and for X-ray diffraction data, a JEOL, model JDX-3080 instrument was used.

3. Results and discussion

3.1. Voltammetric studies

Typical cyclic voltammograms of Ni in acetonitrile containing 3 M AHF and 0.5 M triethylamine at different sweep

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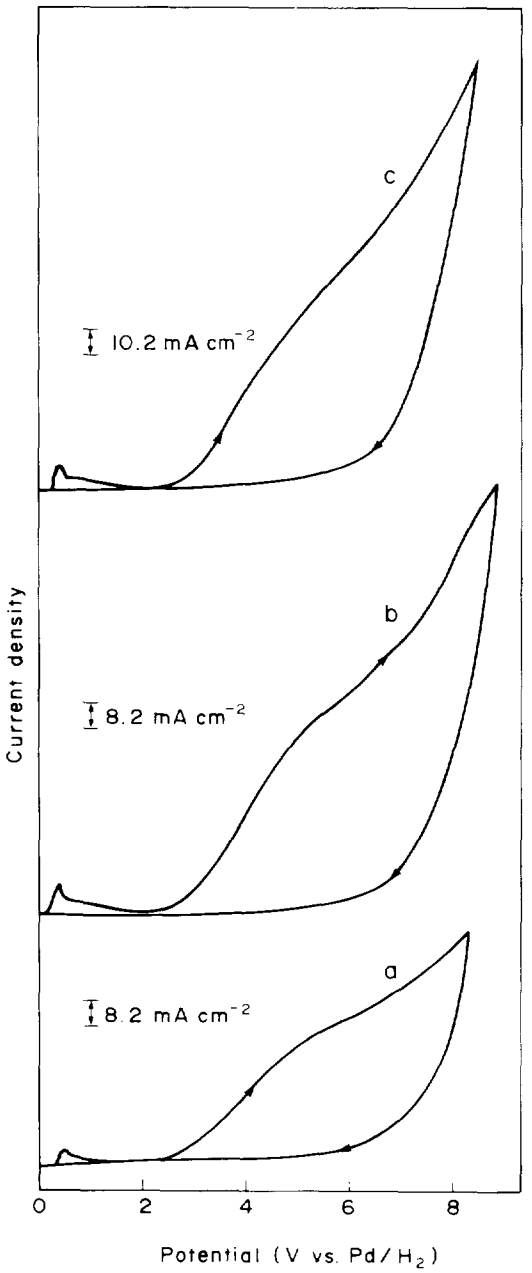

Fig. 1. Cyclic voltammetry of Ni in CH_3CN containing 3 M AHF and 0.5 M triethylamine at sweep rates ($mV\ s^{-1}$) of (a) 60, (b) 120 and (c) 240.

rates are presented in Fig. 1. A small anodic peak current is present below 1 V which is probably due to the formation of a monolayer of NiF_2 film [3]. This is followed by a steadily increasing current beyond 3 V. This second anodic peak current increases significantly with sweep rate. The peak potential for this peak, however, is not distinct. The dissolution charge as measured by integrating the cyclic voltammetric curve decreases with increasing sweep rate (Table 1).

It is interesting to note that the anodic dissolution charge in the 3 M AHF–acetonitrile system alone is much lower when compared to the dissolution charge noted in acetonitrile containing 3 M AHF and 0.5 M triethylamine (Table 1, expt. Nos. 1–3 and 4–6).

When the triethylamine concentration is increased to 1.5 M, significant changes in the main voltammetric peak were noted. The main anodic process is initiated only above 4.5 V in the presence of 1.5 M triethylamine (Fig. 2). A sharp peak followed by a diffused second peak could be observed at all

Table 1
Voltammetric features of Ni in CH_3CN containing 3 M AHF and various concentrations of triethylamine

Expt. No.	Conc. of triethylamine (M)	Sweep rate ($mV\ s^{-1}$)	E_{pf} (V)	i_{pf} ($mA\ cm^{-2}$)	Q_f ($C\ cm^{-2}$)
1	0.0	60	4.0	25.8	0.96
2	0.0	120	4.5	28.2	0.55
3	0.0	240	4.8	33.1	0.40
4	0.5	60	–	–	2.60
5	0.5	120	–	–	2.31
6	0.5	240	–	–	1.32
7	1.5	60	5.0	13.75	0.22
8	1.5	120	5.4	27.51	0.50
9	1.5	240	5.6	30.57	0.41
10	3.0	60	5.5	6.37	0.15
11	3.0	120	5.6	17.83	0.23
12	3.0	240	5.8	26.74	0.30
13	4.5	60	5.1	6.62	0.17
14	4.5	120	5.2	14.33	0.21
15	4.5	240	5.7	33.11	0.45

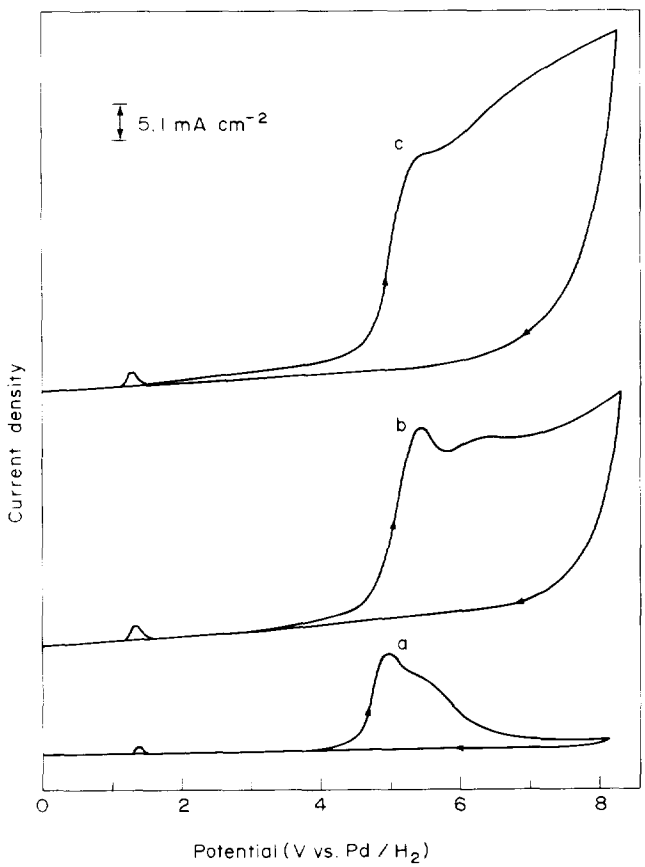

Fig. 2. Cyclic voltammetry of Ni in CH_3CN containing 3 M AHF and 1.5 M triethylamine at sweep rates ($mV\ s^{-1}$) of (a) 60, (b) 120 and (c) 240.

sweep rates. The peak currents increased with sweep rates (Fig. 2, Table 1). The dissolution charge is significantly lower in this medium.

The qualitative voltammetric features do not change significantly on further addition of Et_3N. The anodic peak potentials and peak currents vary slightly. The dissolution charge also decreases slightly (Table 1).

It should be mentioned that in multisweep cyclic voltammetric experiments, no anodic current is noticed in the second and subsequent sweeps in all the above media [1]. The passive films formed in acetonitrile–HF–triethylamine systems are indeed remarkably stable.

The above experimental results suggest that, for anodic dissolution of nickel, acidity as well as a high fluoride concentration are essential. The acidity is required for chemically converting the nickel oxide or nickel hydroxide layer to an electrochemically active oxyfluoride or fluoride layer.

$$Ni(OH)_2 + H^+ + HF_2^- \longrightarrow Ni(OH)F + H_2O + HF \quad (1)$$

In acetonitrile–3 M HF solutions, this chemical initiation reaction is possible to some extent because of the self-dissociation of HF.

$$2HF \longrightarrow H^+ + HF_2^- \quad (2)$$

Addition of triethylamine in a very small molar ratio (say 0.5 M in this case) leads to further dissociation of HF and hence enhanced fluoride concentrations.

$$Et_3N + 2HF \longrightarrow Et_3NH^+ + HF_2^- \quad (3)$$

However, this process decreases the effective HF concentration available for reaction (2). Thus, in acetonitrile–HF solution containing a low molar ratio of triethylamine, while the fluoride ion concentration increases the H^+ concentration decreases. The lower acidity is responsible for the shift of the dissolution potential to more positive values. The increase in fluoride ion concentration is responsible for the higher dissolution as measured by the higher anodic dissolution charge Q_f (Table 1).

On further increase in the molar ratio of triethylamine, reaction (3) completely dominates over reaction (2). Hence, the H^+ concentration is practically completely suppressed. The anodic dissolution process is now initiated only beyond 4.5 V. Since the chemical attack of $Ni(OH)_2$ is also slow, the anodic dissolution charge also decreases significantly.

3.2. Potentiostatic polarisation studies

To evaluate the polarisation effects over extended periods, some potentiostatic polarisation studies were also carried out. These studies also confirmed the trends noticed in cyclic voltammetric measurements. In acetonitrile–3 M AHF solution containing 0.5 M triethylamine, a significantly higher dissolution rate is noticed over extended periods (Fig. 3). The dissolution charge also increases with increasing anodic potential limit (Fig. 3). In acetonitrile–3 M AHF solutions containing 1.5 M (Fig. 4), 3 M and 4.5 M triethylamine, the

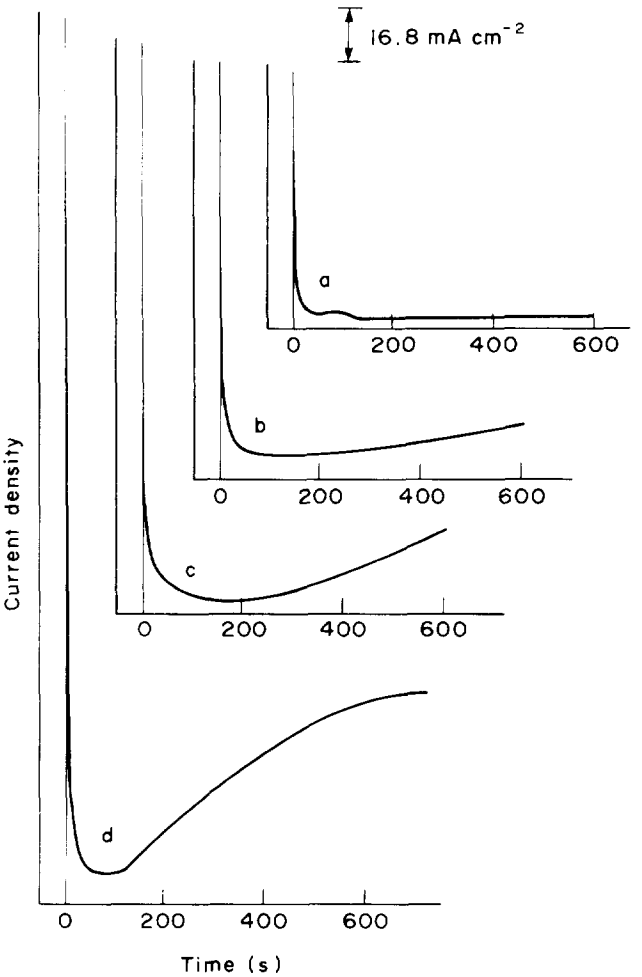

Fig. 3. Current–time curves of Ni in CH_3CN containing 3 M AHF and 0.5 M triethylamine at step potentials (V) from 0.0 to (a) 0.4, (b) 3.0, (c) 5.5 and (d) 6.0.

anodic charge is found to be significantly lower. The anodic charge once again increases with anodic potential limit. Quantitatively, the dissolution charge data obtained from these measurements are summarised in Table 2. The similarities in the trends of dissolution charge values obtained from cyclic voltammetry (Table 1) and the potential–time curves (Table 2) are obvious.

3.3. Microscopic evaluation of surfaces

In concentrated aqueous HF solutions, the nickel electrode surfaces does not undergo significant dissolution when the electrode is not anodically polarised [Fig. 5(a)]. The polished lines on the initially present oxide layer of nickel, punctured mainly on the scratch lines in the form of very small pits, (less than 1 μm) should be noted in this figure [Fig. 5(a)]. In 20 M aqueous HF solutions, significant anodic dissolution is noted even when the electrode is anodically polarised at a minimum anodic potential of +0.4 V for the short period of 5 min [2]. The electrode surface becomes significantly rough, with a very high density of pits [Fig.

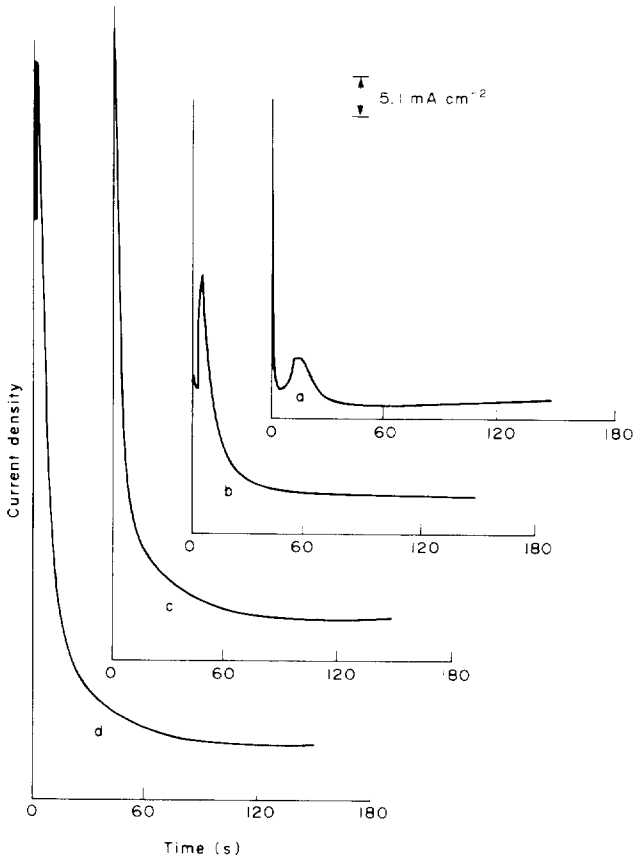

Fig. 4. Current–time curves of Ni in CH_3CN containing 3 M AHF and 1.5 M triethylamine at step potentials (V) from 0.0 to (a) 4.0, (b) 4.5, (c) 5.1 and (d) 6.0.

Table 2
Charge density Q_f and current density i_{pf} values from the current–time curves recorded for 300 s for the anodic polarisation of Ni in CH_3CN containing 3 M AHF and various concentrations of triethylamine

Expt. No.	Conc. of triethylamine (M)	Voltage (V)	i_{pf} for 300 s (mA cm^{-2})	Q_f for 300 s (C cm^{-2})
1	0.0	2.0	16.00	4.10
2	0.0	3.4	6.00	1.80
3	0.0	4.5	17.10	4.50
4	0.5	0.4	5.04	1.09
5	0.5	3.0	13.36	2.60
6	0.5	5.5	47.04	11.50
7	0.5	6.6	63.80	14.20
8	1.5	4.0	1.02	0.30
9	1.5	4.5	1.53	0.38
10	1.5	5.1	10.20	2.80
11	1.5	6.0	5.10	2.20
12	3.0	4.1	0.51	0.58
13	3.0	4.4	1.02	0.63
14	3.0	5.5	2.55	1.27
15	3.0	6.0	1.53	1.14
16	4.5	4.4	0.05	0.03
17	4.5	5.2	0.50	0.13
18	4.5	5.5	1.00	0.45
19	4.5	6.0	0.50	0.38

5(b)]. Some of the pit regions have diameters greater than 20 μm.

The anodic dissolution rate decreases significantly when the anodic polarisation is carried out in acetonitrile containing anhydrous HF (Fig. 6). Even when the electrode is polarised at the fairly high anodic potential of 6 V for fairly long times, dissolution occurs only selectively on the polished lines [Fig. 6(a)]. The pit sizes fall to around 1–10 μm [Fig. 6(b)].

The effect of addition of 3 M water to the acetonitrile AHF medium leads to significantly enhanced anodic dissolution [Fig. 6(c) and (d)]. The oxide layer now contains a fairly high concentration of pits [Fig. 6(c)]. The pit size is generally found to be around 10 μm [cf. Fig. 6(a) and (d) at the same magnification]. The similarity between the pitting patterns of anodically polarised surfaces in 20 M aqueous HF solution and acetonitrile–3 M HF solution containing 3 M water, [cf. Fig. 5(b) and Fig. 6(d) at the same magnification] is quite apparent, although the pit intensity is much smaller in the latter media as one would expect. This suggests that as long as significant water is present, the anodic dissolution follows practically the same type of overall dissolution–precipitation pathway. A lower fluoride concentration and the presence of non-aqueous solvent only shifts the anodic potential for the dissolution film formation process.

The anodic dissolution behaviour in acetonitrile–3 M AHF solution containing triethylamine is significantly different (Fig. 7). The dissolution behaviour in acetonitrile–3 M AHF containing 0.5 M triethylamine is quite interesting. In this

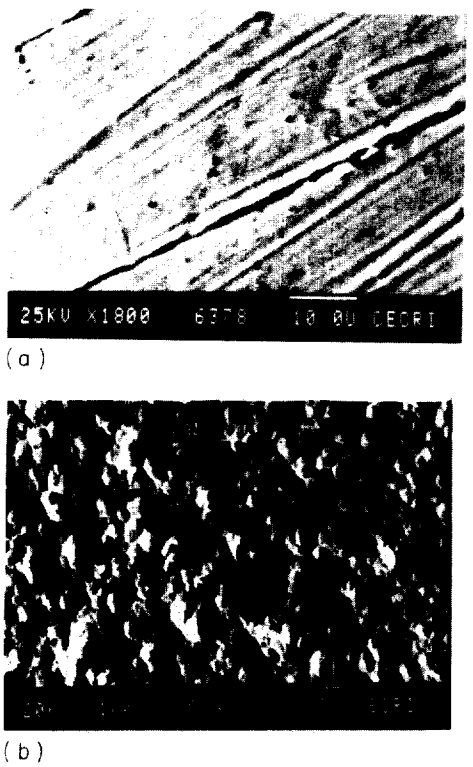

Fig. 5. Scanning electron micrographs of Ni in 20 M aqueous HF: (a) after dipping for 5 min under open circuit potential (×1800); (b) after anodic polarisation for 5 min at 400 mV (×1000).

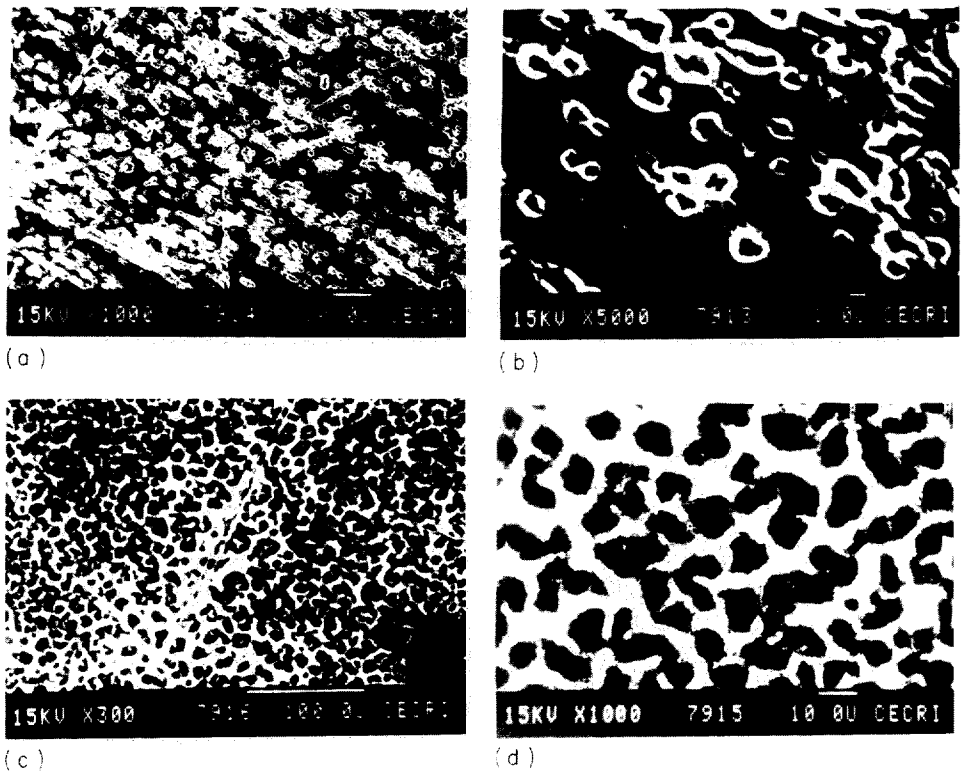

Fig. 6. (a and b) Scanning electron micrographs of Ni in CH_3CN containing 3 M AHF after anodic polarisation for 5 min at 6 V [(a) ×1000 and (b) ×5000]; (c and d) scanning electron micrographs of the same solution in the presence of 3 M water under the same conditions [(c) ×300 and (d) ×1000].

medium, dissolution seems to proceed uniformly throughout the surface. The roughness on the oxide layer noted for the fresh electrode in Fig. 5(a) practically disappears after polarisation in this medium [cf. Fig. 5(a) and Fig. 7(a)]. Some small pits however are still noted on the scratch lines.

In acetonitrile–3 M AHF containing higher concentrations of triethylamine, pit formation is not predominant. A different type of film growth pattern is noted here. A typical microscopic response in acetonitrile–3 M AHF solution containing 4.5 M triethylamine is presented in Fig. 7(b). Independent nodules of salt crystallites are noted on the nickel surface after polarisation in this medium [Fig. 7(b)]. The size of the nodules may grow to 15 μm. The salt layer grows around some active centres on the nickel surface which may probably be the pits formed on the oxide layer of nickel. The salt nodules also possess sharp edges, cracks and hollow regions [Fig. 7(b)] suggesting that they are indeed quite different from the oxide layers and pitted regions noted after polarisation in aqueous solutions [Fig. 5(b)].

3.4. Diffraction studies

Some XRD studies were also carried out to identify the crystalline faces formed on nickel electrode during polarisation. In aqueous solutions, polarisation of the electrode surface for 30 min is sufficient for identifying significant XRD features. In acetonitrile–AHF based systems, electrode polarisation for 2 h was found to be necessary for observing XRD signals. XRD results indicate the formation of $NiF_2 \cdot 4H_2O$ on the electrode surface in all the media studied (Table 3).

Table 3
XRD features of Ni surface after anodic polarisation in different fluoride media

Expt. No.	Sample	I/I_0 at		
		4.85 (Å) [a]	4.10 (Å) [a]	3.14 (Å) [b]
1	20 M aqueous HF	17	–	–
2	3 M AHF–CH_3CN	–	–	–
3	3 M AHF–CH_3CN–3 M H_2O	24	15	16
4	3 M AHF–4.5 M Et_3N–CH_3CN	27	–	18
5	3 M AHF–4.5 M Et_3N–CH_3CN–3 M H_2O	43	28	28

[a] Characteristics of $NiF_2 \cdot 4H_2O$.
[b] Not characterised.

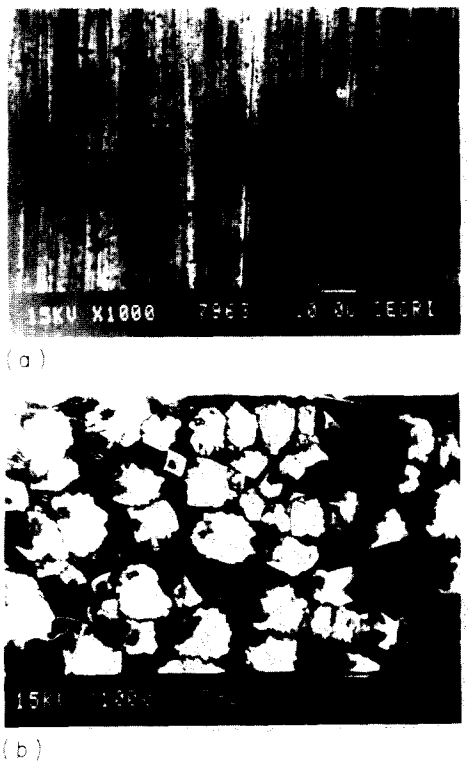

Fig. 7. Scanning electron micrographs of Ni in CH_3CN containing 3 M AHF and (a) 0.5 M (b) 4.5 M triethylamine after anodic polarisation for 5 min at 7.0 V (× 1000).

The signal intensity was found to be higher whenever the water content in the electrolyte medium was increased (Table 3). The presence of $NiF_2 \cdot 4H_2O$ is characterised by the *d*-values of 4.85 Å and 4.10 Å [4]. It is quite interesting to note that formation of this phase occurred even in acetonitrile AHF–solution, which is essentially free from water but may contain a trace level of water in the electrolyte medium. Another possibility is the absorption of water during the storage and transfer of the NiF_2 film covered electrodes from the electrochemical cell to the XRD measurement system.

An additional XRD signal is also noted at a *d*-value of 3.14 Å. This signal does not belong to any well-characterised NiF_2 or NiO layer. However, it is possible that this is due to an oxyfluoride salt. This assumption however needs further evidence. Such oxyfluoride layers have been characterised by ESCA measurements in aqueous solution by earlier workers [5].

4. Conclusions

The present investigations clearly indicate the role of solvent (water and acetonitrile) and the acid–base properties of the electrolyte media (triethylamine and AHF–mixtures of different molar ratios) on the anodic polarisation of nickel in fluoride media. In anhydrous HF media the anodic dissolution increases with HF concentration.

In acetonitrile–anhydrous HF solutions, addition of triethylamine in small molar ratios enhances the uniform dissolution of the nickel surface due to a higher fluoride concentration and the presence of H^+ ions. When the triethylamine concentration is enhanced, the anodic dissolution proceeds through a different pathway leading to the formation of small nodules of a salt layer on the nickel electrode surface. XRD data suggest that in all cases a $NiF_2 \cdot 4H_2O$ crystalline phase is formed on the electrode surface. An additional XRD signal observed may be possibly attributed to the formation of an oxyfluoride layer.

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