JOURNAL OF APPLIED ELECTROCHEMISTRY **10** (1980) 649–654

Influence of frequency of alternating current on the electrochemical dissolution of mild steel and nickel

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Received 24 September 1979

The electrochemical dissolution of mild steel and nickel in hydrochloric acid and sulphuric acid has been studied with alternating current of varying frequencies. For both mild steel and nickel the current efficiency decreases exponentially with increasing frequency. With increasing current density (32 to 100 mA cm^{-2}) and increasing acid concentration (0.5 to 2.0 N), the current efficiency increases. Mild steel is dissolved more efficiently in sulphuric acid than hydrochloric acid but the reverse is true for nickel.

1. Introduction

It is well known that in the corrosion of metals unidirectional currents are involved. However, under certain conditions, alternating currents (a.c.) can also cause corrosion although at a lower rate than direct currents. A review of the literature reveals that a number of investigations have been carried out on the a.c. corrosion of iron, lead, copper, aluminium and other metals [1–4]. Besides the corrosion of metals, the dissolution of metals by a.c. has also attracted the attention of a number of investigators [5–8].

It has been reported that the frequency of the a.c. has an important effect on the rate of the dissolution of metals. The dissolution of mild steel by a.c. at various frequencies from 20 to 1000 Hz has been studied [2, 4]. It has been reported that copper electrodes in KCN solution are completely dissolved when a.c. of 16 Hz is applied but they cease to dissolve completely at higher frequencies, say 1000 Hz [9]. The influence of a.c. frequency on the passivation of titanium has been investigated [10]. In the present investigation, the effect of the frequency of sine wave a.c. on the electrochemical dissolution of mild steel and nickel has been studied.

2. Experimental

All experiments were carried out in a glass beaker. Electrodes of rectangular shape (5 cm × 3 cm) were used. The spacing between the electrodes was maintained at 2 cm. The volume of the electrolyte used was 200 ml for each experiment. The electrolyte was stirred by means of a magnetic stirrer. All the experiments were carried out at room temperature (30° C).

The a.c. frequency was varied with an audio and ultrasonic frequency signal generator (Type Г3-33 made in USSR). The frequency was varied from 25 Hz to 2000 Hz. The current was measured by means of a digital multimeter (APLAB Model 1005).

2.1. *Current efficiency under a.c. conditions*

The current efficiency for a.c. conditions was calculated by a weight loss method. The part of the alternating current which is actually utilized in the electrolysis is the average value or d.c. equivalent, denoted as I_{avg}. This can be calculated from the relation,

$$I_{\text{avg}} = \frac{2\sqrt{2}}{\pi} I_{\text{rms}}$$

where I_{rms} is the current indicated by an a.c. ammeter.

If Q is the quantity of electricity (where $Q = I_{\text{avg}} \times t$ and t is the time of electrolysis) used for the electrolysis, then the weight of the metal (m') that would dissolve theoretically at 100% efficiency is

$$m' = \frac{Q}{F}\frac{A_{\text{w}}}{n}$$

where F = Faraday, A_{w} = Atomic wt of metal,

0021–891X/80/050649–06$02.60/0

n = number of electrons involved in dissolution reaction. Hence

$$m' = \frac{2\sqrt{2}I_{\mathrm{rms}}tA_{\mathrm{w}}}{\pi nF}.$$

If m is the actual loss in weight of metal during the electrolysis, the current efficiency is calculated as

$$\text{C.E. (\%)} = \frac{m}{m'}\,100.$$

3. Results

Table 1 shows the experimental results for the electrodissolution of nickel in sulphuric acid. From Table 1, it may be seen that as the a.c. frequency increases, the current efficiency drops. Beyond about 200 Hz it is seen that the other experimental variables such as current density and acid concentration do not have a significant effect on the current efficiency. For frequencies up to 200 Hz, it is seen that the efficiency increases with increasing current density and acid concentration.

The results obtained for nickel dissolution in hydrochloric acid are given in Table 2. In general the results for nickel dissolution in hydrochloric acid are similar to those obtained with sulphuric acid. However, it can be seen that the current efficiency in hydrochloric acid is higher than that in sulphuric acid especially for the lower value of current density (32 mA cm^{-2}).

The experiments with mild steel yielded results similar to those obtained with nickel, the current efficiency decreasing with increasing frequency of a.c. The significant differences in behaviour observed between mild steel and nickel were,

(i) mild steel dissolved electrochemically more efficiently in sulphuric acid than in hydrochloric acid. For nickel the reverse was found;

(ii) the current-efficiency peaks for mild steel (at 25 Hz) were always higher than those for nickel at the same frequency.

The results for the dissolution experiments with mild steel in H_2SO_4 and HCl are shown in Tables 3 and 4, respectively. Fig. 1 shows a comparison of the behaviour of mild steel and nickel in 1 N sulphuric acid at a current density of 100 mA cm^{-2}. A comparison of the behaviour of mild steel and nickel in H_2SO_4 and HCl at different concentrations is displayed in Fig. 2. The figure is drawn for one particular frequency (50 Hz) and one current density (32 mA cm^{-2}).

4. Discussion

When a.c. is passed through the cell containing nickel electrodes in sulphuric acid, the following reactions can occur at the electrode 1, in the positive half-cycle

$$\mathrm{Ni} \rightarrow \mathrm{Ni}^{2+} + 2\mathrm{e} \tag{1}$$

$$2\mathrm{OH}^- \rightarrow \mathrm{H_2O} + \tfrac{1}{2}\mathrm{O_2} + 2\mathrm{e} \tag{2}$$

During this interval the other electrode acts as a cathode and the following reactions can occur at that electrode:

$$\mathrm{Ni}^{2+} + 2\mathrm{e} \rightarrow \mathrm{Ni} \tag{3}$$

$$\mathrm{H}^+ + \mathrm{e} \rightarrow \tfrac{1}{2}\mathrm{H_2}. \tag{4}$$

If the electrolyte is hydrochloric acid, the follow-

Table 1. Current efficiency (%) for the dissolution of nickel in sulphuric acid as a function of acid concentration, current density and a.c. frequency

Acid concentration (N)	*Current density* (mA cm^{-2})	*a.c. frequency* (Hz)						
		25	50	100	200	500	1000	2000
0.5	32	65.2	50.0	9.0	9.0	7.3	5.4	4.5
	64	70.9	53.1	14.1	9.5	7.7	5.6	5.6
	100	73.7	56.2	20.2	10.5	7.7	7.9	6.3
1.0	32	71.4	57.3	19.2	7.4	4.0	3.6	3.5
	64	88.9	75.3	53.6	14.7	3.0	3.2	3.3
	100	89.5	77.2	55.1	19.3	5.2	4.2	3.7
2.0	32	75.1	63.7	29.5	14.8	5.2	4.5	4.4
	64	85.4	74.2	54.5	18.3	6.2	5.7	5.1
	100	90.4	78.7	57.2	20.7	7.5	5.0	6.0

Table 2. Current efficiency (%) for the dissolution of nickel in hydrochloric acid as a function of acid concentration, current density and a.c. frequency

Acid concentration (N)	*Current density* (mA cm^{-2})	*a.c. frequency* (Hz)						
		25	50	100	200	500	1000	2000
0.5	32	72.0	55.1	9.3	9.0	6.5	5.8	3.7
	64	74.0	56.0	15.5	9.8	7.3	6.2	5.7
	100	76.8	63.4	25.4	10.2	8.1	8.0	6.8
1.0	32	80.5	68.7	26.3	13.3	9.1	5.0	3.5
	64	85.1	74.8	60.1	20.1	10.0	5.5	3.6
	100	89.0	85.1	62.3	25.4	10.5	6.0	4.2
2.0	32	86.0	72.4	30.1	22.2	9.8	5.7	4.9
	64	90.3	78.1	60.3	25.5	10.1	5.5	5.4
	100	92.1	88.0	65.4	28.3	12.9	7.0	5.9

ing additional reaction can occur in the anodic half-cycle:

$$2Cl^- \rightarrow Cl_2 + 2e. \qquad (5)$$

For mild steel, the following reactions can occur in the anodic half-cycle for the electrode 1;

$$Fe \rightarrow Fe^{2+} + 2e \qquad (6)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e. \qquad (6a)$$

In addition to these, Reaction 2 also occurs.

At the other electrode, Reactions 6 and 6a occur in the reverse direction and hydrogen evolves according to Reaction 4.

In the next half-cycle, the situation at the electrodes will be exactly the reverse, electrode 1 acting now as cathode and electrode 2 as anode.

For ideal dissolution, Reaction 1 or 6 should occur in the positive half-cycle and only hydrogen evolution (Reaction 4) in the cathodic half-cycle.

From the experimental results, it can be seen that at lower frequencies the metal dissolution is, in general, more efficient which may be explained as follows. In anodic half-cycles, the gas evolution reactions (O_2 or Cl_2) are less likely to take place than the metal dissolution reaction, because of potential considerations. Similarly, in the cathodic half-cycles, the H_2 evolution is more likely than metal deposition.

The rates of these electrochemical reactions may be expressed, in general, in terms of current density, i, by use of the Tafel relationship as follows:

$$i^{M} = i_0^{M} \exp\left(-\alpha^{M}\eta^{M}F/RT\right)$$

$$i^{G} = i_0^{G} \exp\left(-\alpha^{G}\eta^{G}F/RT\right)$$

Table 3. Current efficiency (%) for the dissolution of mild steel in sulphuric acid as a function of acid concentration, current density and a.c. frequency

Acid concentration (N)	*Current density* (mA cm^{-2})	*a.c. frequency* (Hz)						
		25	50	100	200	500	1000	2000
0.5	32	87.9	81.5	73.0	51.9	22.7	8.8	5.5
	64	88.4	82.2	73.5	52.1	23.0	8.8	6.0
	100	85.1	79.7	70.9	47.8	21.3	7.5	4.9
1.0	32	92.9	87.4	77.7	56.7	25.4	12.3	8.0
	64	84.6	87.4	76.5	55.2	27.9	9.3	7.4
	100	85.1	82.0	74.7	53.5	25.1	9.0	5.9
2.0	32	95.1	87.5	77.8	59.3	27.0	10.1	7.2
	64	96.5	88.1	79.2	60.0	27.8	10.9	8.3
	100	89.4	84.2	75.0	56.2	26.0	9.2	6.0

Table 4. Current efficiency for the dissolution of mild steel in hydrochloric acid as a function of acid concentration, current density and a.c. frequency

Acid concentration (N)	*Current density* (mA cm^{-2})	*a.c. frequency* (Hz) 25	50	100	200	500	1000	2000
0.5	32	77.7	67.3	50.9	40.9	13.1	5.9	4.2
	64	81.5	70.9	60.1	42.3	14.5	7.5	5.0
	100	84.1	75.5	61.9	44.5	15.2	8.7	6.0
1.0	32	80.5	74.6	47.2	43.4	10.6	7.0	4.1
	64	82.9	76.2	57.1	43.6	12.7	8.0	4.9
	100	90.3	90.1	61.0	43.5	13.2	7.5	5.0
2.0	32	90.0	85.1	60.4	40.3	10.5	7.0	3.9
	64	95.1	86.9	64.4	41.2	11.0	7.4	4.1
	100	95.0	88.7	65.0	44.3	11.1	7.5	4.2

where, M is the metal (Ni or Fe in this case) and G is the gas (H_2, O_2 or Cl_2 in this case), i is actual current density, i_0 is the exchange current density, determined by the composition of the electrolyte. α is the transfer coefficient, T is the temperature, F and R are the usual constants, and η is the overvoltage required for anodic or cathodic reaction. The total current density $I_{avg} = i^M + i^G$.

In an anodic cycle, i^M is the current utilized for metal dissolution and i^G is for gas evolution (O_2 or Cl_2 as the case may be). It may be assumed that the major part of I_{avg} would be consumed for

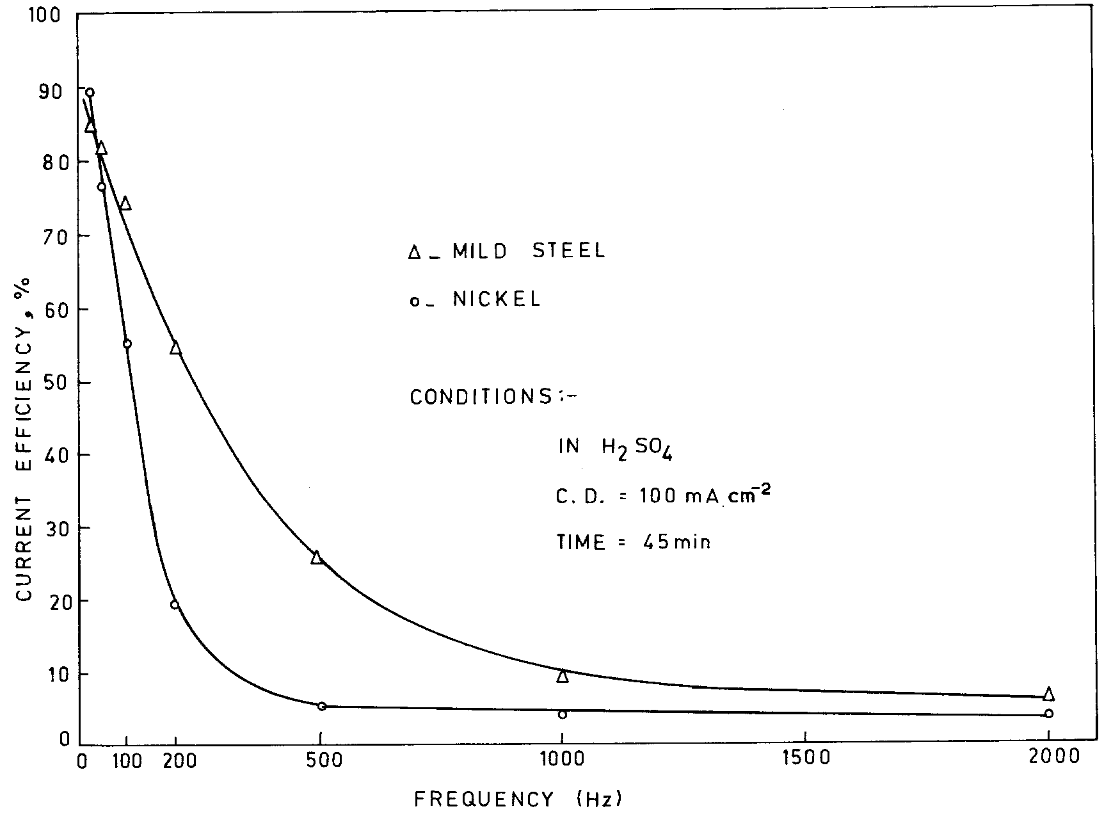

Fig. 1. Comparison of dissolution of nickel and mild steel in H_2SO_4.

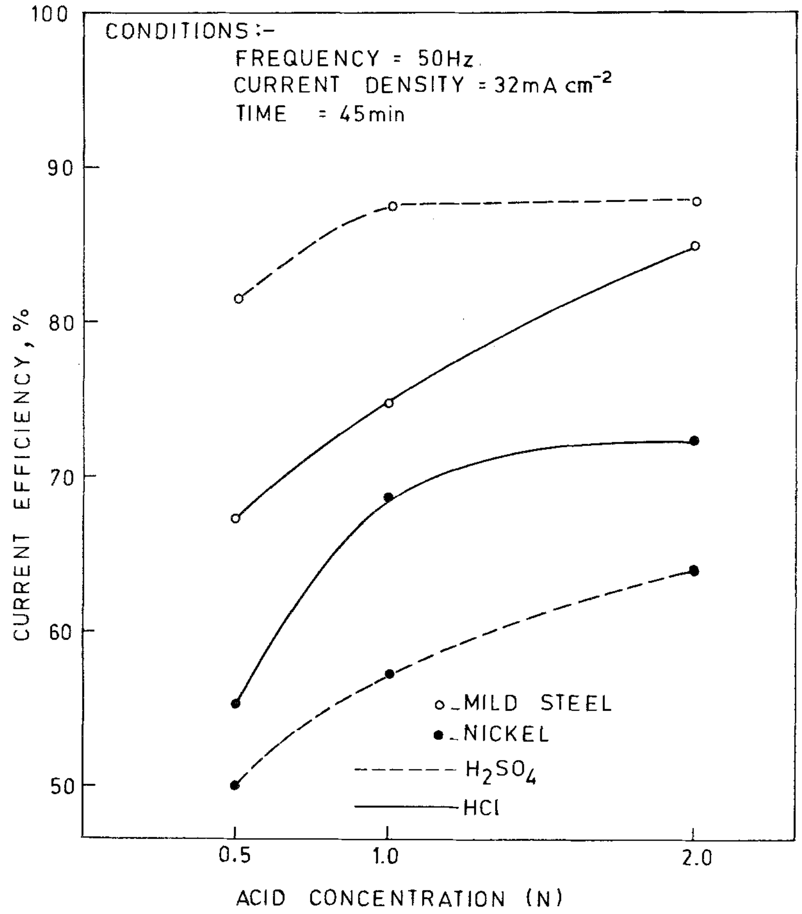

Fig. 2. Comparison of dissolution of nickel and mild steel with respect to acid concentration.

metal dissolution. O_2 or Cl_2 evolution will only take place under the conditions of concentration polarization, which is unlikely to take place under the efficient stirring conditions provided in the experiment.

In cathodic cycles, i^M is the current for metal deposition and i^G, for H_2 evolution. However, in this case, the major part of the I_{avg} would be utilized for H_2 evolution. This is because Ni or Fe require higher deposition potentials associated with high overvoltages.

Thus the quantity of electricity expended for dissolution of metal in the anodic cycle must be greater than the quantity of electricity expended for metal deposition in the cathodic cycle. This is actually observed experimentally at lower frequencies.

With increasing a.c. frequency, the interval between successive anodic and cathodic half-cycles becomes progressively shorter. Under these conditions, less metal will dissolve comparatively. Also, as time interval is short, the metal ions formed at the electrode in anodic cycles would be available for immediate redeposition in the cathodic cycles. In addition to this, at higher frequencies, the hydrogen atoms formed in the cathodic half-cycle do not have time to coalesce and form hydrogen gas molecules. Thus for the next anodic cycle there exists a layer of hydrogen atoms on the electrode surface, which prevents the metal dissolution reaction to some extent and the hydrogen ionization reaction takes place instead. With increasing frequency this effect intensifies. Hence, at higher frequencies, the current efficiency falls. At very high frequencies, no effects of a.c. would be observed, since all current would pass via the double layer.

The lower efficiency of nickel dissolution in dilute acids is apparently the consequence of the formation of insoluble oxide films on the electrode surface during the positive half-cycle. With increase in the acid concentration, the passivating effect of such films decreases owing to the ability of the more concentrated acid to dissolve the oxide film.

At higher current densities, the efficiency for nickel dissolution is higher. This may be due to the fact that the higher oxides of nickel are reduced to lower oxides which dissolve in the electrolyte. It is also possible that the passivating layer of nickel oxide is reduced to nickel ions according to the following reaction:

$$NiO_2 \cdot 2H_2O + 4H^+ + 2e \rightarrow Ni^{2+} + 4H_2O,$$

which will expose fresh nickel surface for subsequent dissolution. The efficiency for nickel dissolution is higher in HCl than that in H_2SO_4. This can be attributed to the breaking up of passivating nickel oxide film by chloride ions.

Mild steel exhibits a behaviour similar to nickel with respect to current density, acid concentration and frequency. However, its dissolution efficiency is lower with hydrochloric acid than with sulphuric acid.

References

[1] F. E. Kulman, *Corrosion* 17 (3) (1961) 34.
[2] A. R. Yamuna and N. Subramanyam, *ibid* 23 (9) (1967) 264.
[3] C. I. Galimberti, *ibid* 20 (5) (1964) 150.
[4] N. D. Tomoshov and N. M. Strukov, *Korroz. Zashch Konstr. Splavov, Akad. Nauk. SSSR, Inst. Fiz. Khim* (1966) 58, cited in *Chem. Abs.* 67 (1967) 49, 788k.
[5] M. J. Reuben and S. Venkatachalam, *J. Appl. Electrochem.* 8 (1978) 293.
[6] A. D. Styrkas and O. N. Efimov, *J. Appl. Chem. USSR* 43 (1970) 170.
[7] A. I. Ryaznov, G. D. Petroenko and E. G. Domanova, *ibid* 43 (1970) 890.
[8] K. Deo, S. G. Mehendale and S. Venkatachalam, *J. Appl. Electrochem.* 6 (1976) 37.
[9] G. Kortum, 'Treatise on Electrochemistry, Elsevier, London (1965) p. 494.
[10] N. D. Tomashov and N. M. Strukov, *Chem. Abs.* 60 (1966) 37136.