

Influence of temperature on the electro-dissolution of tin in NaCl aqueous solution at pH4

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The influence of temperature in the range 25 to 80°C on the dissolution of tin was investigated in an acidic solution at pH4 containing 0.1 to 1 M NaCl. The corrosion current is slightly dependent on both the temperature and the Cl⁻ ion concentration. The main dissolution characteristics of tin are

$$\left(\frac{\partial E}{\partial \log i} \right)_{\text{Cl}^-} \approx \frac{2}{3} \frac{RT}{F} \quad \left(\frac{\partial \log i}{\partial \log a_{\text{Cl}^-}} \right) \approx i$$

with an apparent energy of activation of 33 kJ mol⁻¹ as long as the electrode surface is bare, whence it is deduced that the dissolution process is the same over the entire range of temperatures and concentrations under consideration. The behaviour of tin is different when a precipitate is formed on its surface, which is generally observed at $E > -0.5V_{\text{sce}}$. The changes occurring on the electrode surface were observed by semi-quantitative energy dispersive X-ray analysis and scanning electron microscopy.

1. Introduction

Copper, steel and nickel in many applications may be coated with tin or lead-tin alloys, which serve as sacrificial metals. This raises an interest in the corrosion kinetics of tin. Electric equipment can undergo a temperature rise in operation which may affect the corrosion kinetics. Despite this no studies of the influence of temperature on the corrosion of tin have been reported in the literature, yet the dissolution mechanisms for other metals, e.g. copper [1-3], are found to be largely dependent on temperature.

Recently, we investigated the anodic dissolution of tin in an acidic solution at pH4 containing 0.1 to 1 M NaCl at 25°C [4]. Tin anodes display a Tafel behaviour as long as the electrode surface is bare ($E < -0.5V_{\text{sce}}$). A dissolution mechanism comprising two consecutive steps was suggested, each corresponding to the transfer of one electron, with the second step being rate-determining. For E values anodic to $-0.5V_{\text{sce}}$, however, partial coverage of the surface by a corrosion product is reported and the behaviour is no longer Tafelian. The study reported here investigates the effect of temperature (25-80°C) on anodic tin dissolution as a function of potential, time and concentration (0.1 to 1 M) of NaCl solutions at pH4. A rotating-disc electrode is used. The changes occur-

ring on the electrode surface are characterized by semi-quantitative energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM) and Auger electron spectroscopy (AES).

2. Experimental method

The measurements were made in a conventional two-compartment, three-electrode electrochemical cell using a rotating-disc electrode cut from a polycrystalline tin rod (Johnson Matthey Chemicals Ltd, grade 1) and set in a Kel-F holder. The speed of rotation was maintained at 1000 rpm. The electrode surface (0.13 cm²) was polished with an alumina suspension and rinsed with distilled water. The auxiliary electrode was a platinum grid separated from the main compartment. All potentials quoted in this paper are given against the saturated calomel reference electrode at 25°C and connected to the main compartment by a bridge with a Luggin capillary. The working and reference electrodes were maintained at different temperatures; the measured potentials therefore contain a junction potential partly due to the temperature gradient. The main compartment was held at constant temperature by circulating thermostated water.

Solutions of 0.1 to 1 M NaCl (Baker analysed reagent grade) were prepared and set at pH4 using

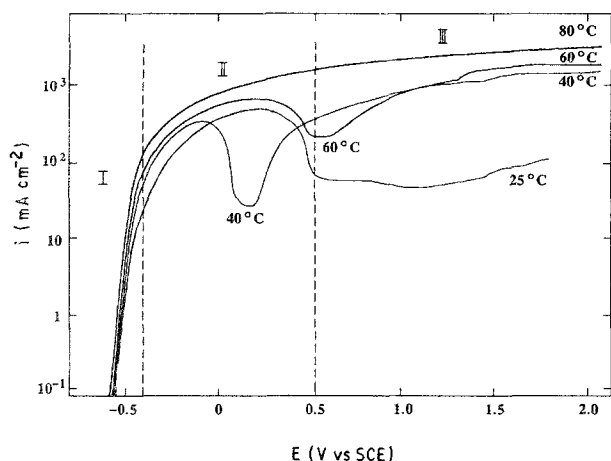


Fig. 1. Typical anodic polarization curves, $\log i$ against E , for a rotating-disc electrode at 1000 rpm in 1 M NaCl solution at pH4 and temperatures: 25, 40, 60 and 80°C. The potential sweep rate is 10 mV s^{-1} . I is the Tafel region; II the maximum current region; III the limiting current plateau region.

HCl. No buffer or support electrolyte was used. Before each measurement, the solution was deaerated with a flow of nitrogen, which was maintained throughout the experiment. The measurements were carried out at 25–80°C.

The potential applied to the working electrode by a PAR 273 potentiostat was controlled by a pulse generator with a fast rise time PAR 175 universal programmer. The current-time transients were recorded under Commodore PCII microcomputer control using a GPIB-PC-2A interface and for microsecond records, a Computerscope interface (RC Electronic Inc.). Electrode rotation was performed using an Analytical Rotator Pine Instrument.

3. Results and discussion

The tin electrode was first immersed in the solution with the potentiostat at -0.8 V to remove any surface

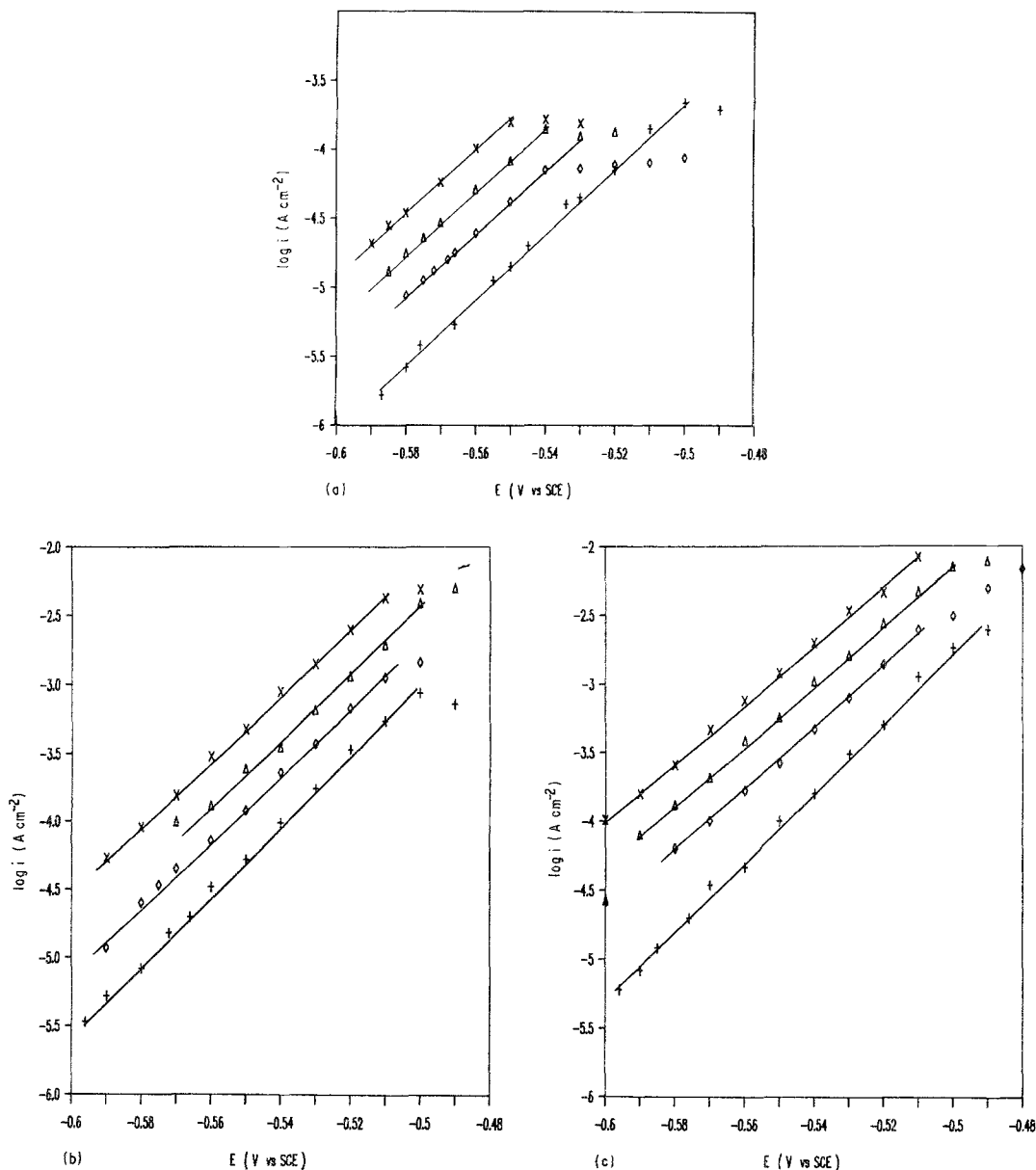


Fig. 2. The influence of temperature on $\log i$ against E curves at $\omega = 1000 \text{ rpm}$: +, 25°C; ◇, 40°C; △, 60°C; ×, 80°C, for different NaCl concentrations: (a) 0.1 M; (b) 0.5 M; (c) 1 M.

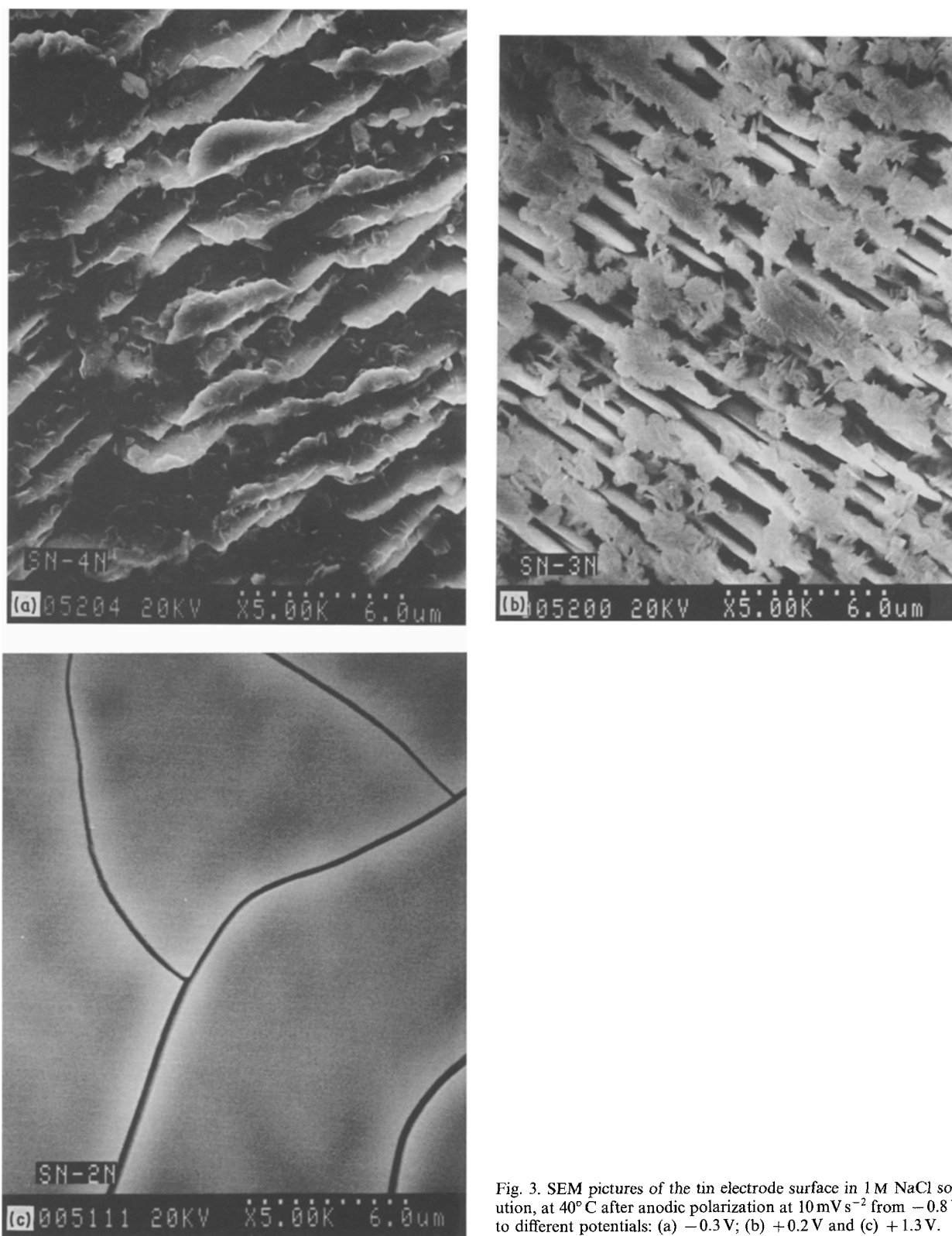


Fig. 3. SEM pictures of the tin electrode surface in 1 M NaCl solution, at 40°C after anodic polarization at 10 mV s^{-2} from -0.8 V to different potentials: (a) -0.3 V ; (b) $+0.2 \text{ V}$ and (c) $+1.3 \text{ V}$.

oxides and then it was left on open-circuit. The corrosion potential reached steady values in about 5 min (Table 1) but as the temperature increased the reproducibility deteriorated.

The electrochemical behaviour of tin in 1 M NaCl pH4 solutions at different temperatures is illustrated, in Fig. 1 by the polarization curves for a polycrystalline tin electrode rotated at 1000 rpm with a potential sweep rate of 10 mV s^{-1} . The curves may be arbitrarily divided into three regions: I, an exponential current-

potential region (i.e. Tafel behaviour); II, a current maximum region; and III, a large limiting current-plateau region.

The general trend is that the open-circuit potential and the polarization curves shift towards more cathodic values as the temperature increases. The temperature has only a moderate influence on the Tafel slope, which is $\approx \frac{2}{3} RT/F$, from which it is deduced that the tin dissolution mechanism does not vary with temperature in the Tafel region. As the applied poten-

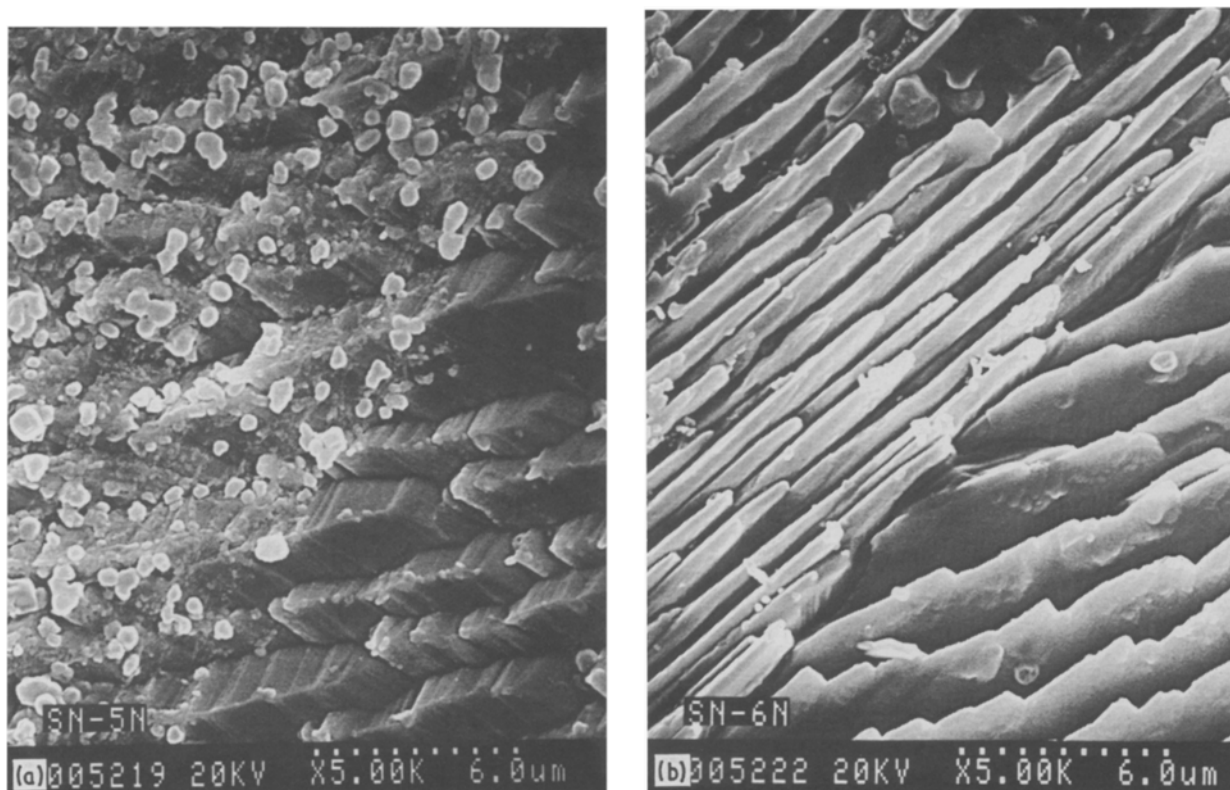


Fig. 4. SEM pictures of the tin electrode surface in 1 M NaCl solution, at 80°C after anodic polarization at 10 mV s⁻¹ from -0.8 V to different limits of potentials: (a) -0.3 V and (b) +1.3 V.

tial becomes sufficiently high, the behaviour differs from the Tafelian and a plateau current region is observed. The plateau current increases significantly from 25 to 80°C.

3.1. Tafel region

To investigate the anodic dissolution of tin at various temperatures, anodic current as a function of potential, time, temperature and NaCl concentration was measured. The current-time curves at different values of the applied constant potential were recorded by

computer. The potential step starts from the open-circuit potential to the desired anodic potential. The surface is seen to darken during anodic polarization of tin in the Tafel region. The nature of the changes occurring was investigated by optical and SEM methods. The black spots observed are rough compared to the rest of the surface.

The steady-state current density values were obtained and the log i against E curves at 1000 rpm were plotted. The dissolution is more pronounced at the grain boundaries and the tin is free of corrosion products. The latter characteristic supports the fact that the

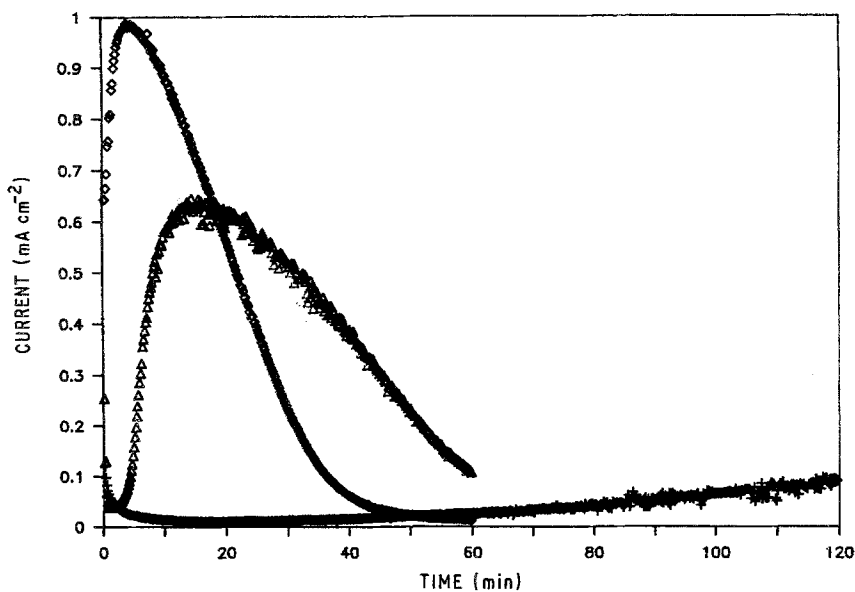


Fig. 5. Current against time transients in 0.1 M NaCl solution at -0.45 V at three temperatures: +, 25°C; Δ, 60°C and ◇, 80°C.

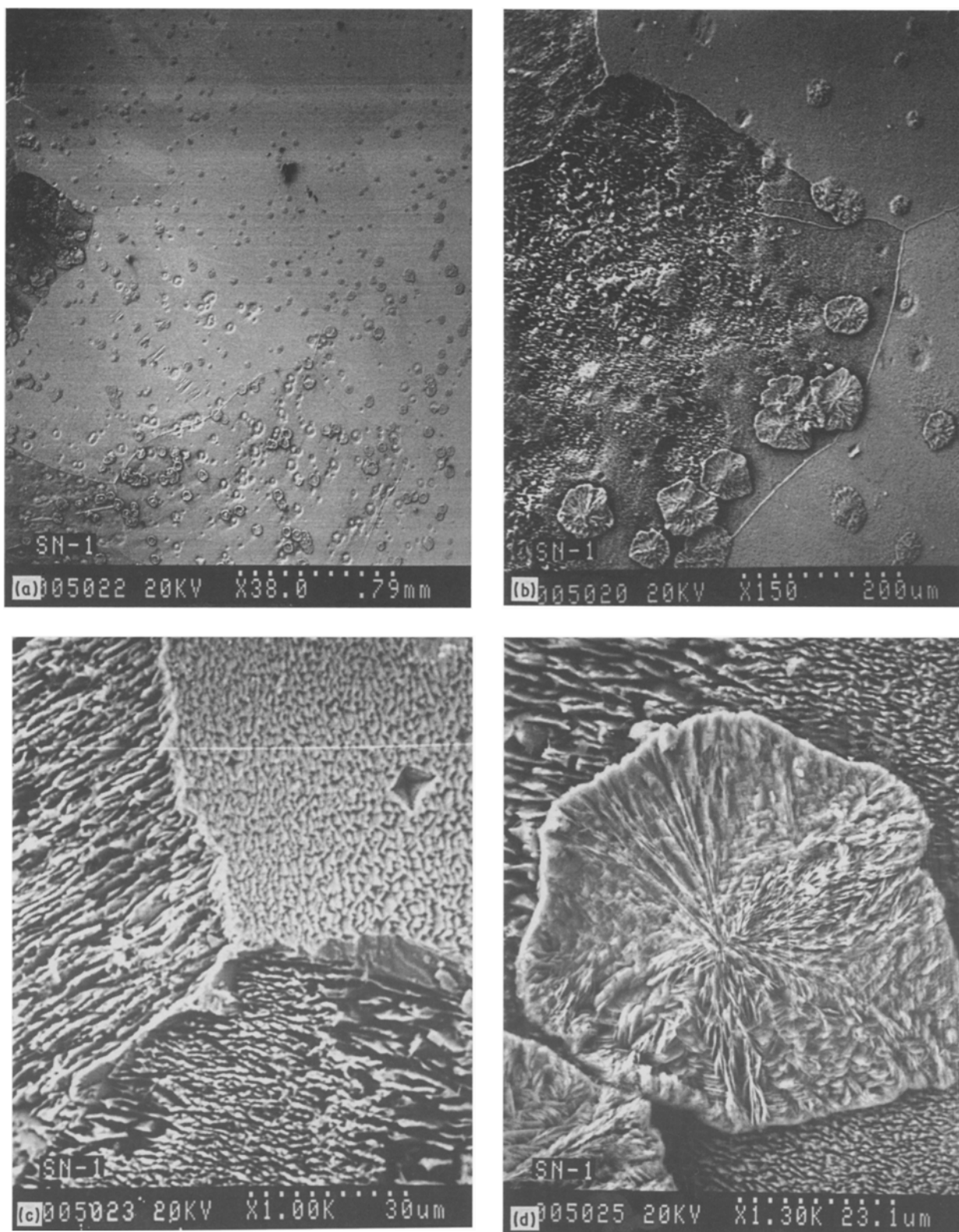


Fig. 6. SEM pictures of the tin electrode surface after 2 h of experiment at 25°C and -0.45 V in 0.1 M NaCl solution; magnification (a) 38 \times ; (b) 150 \times ; (c) 1000 \times ; (d) 1300 \times .

current density remains constant after several seconds' polarization at a given applied potential in the Tafel region. In Fig. 2 the results at different temperatures are presented for 0.1 M (Fig. 2a), 0.5 M (Fig. 2b) and 1 M (Fig. 2c) NaCl solutions.

The Tafel behaviour for each temperature and NaCl concentration is observed over at least one, often two, decades of current density. The slopes

remain practically constant, between 40 and 47 mV dec^{-1} (Table 1), i.e. $\approx \frac{2}{3} RT/F$ and the order of reaction with respect to the Cl^- ion activity is approximately 1.

The different energies of activation associated with the electrochemical reactions can be deduced from an Arrhenius plot. The apparent energy of activation at different polarization potential, in the Tafel region, is

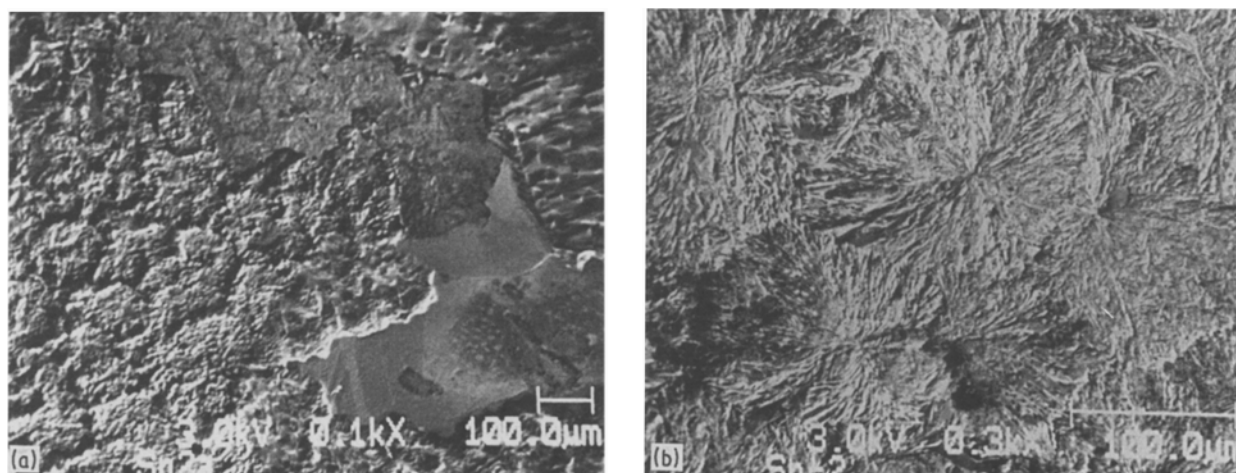
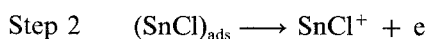
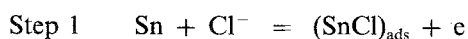


Fig. 7. SEM picture of the tin electrode surface after 1 h of experiment at 80°C and -0.45 V in 0.1 M NaCl solution; magnification: (a) 100 \times ; (b) 300 \times .

close to 33 kJ mol^{-1} , a value which is independent of the applied potential and chloride anion concentration. These results are in good agreement with the dissolution mechanism proposed earlier [4]. The process involved the surface formation of chemisorbed $(\text{SnCl})_{\text{ads}}$ species as the intermediate (Step 1), whereas the rate determining Step (rds) corresponds to the electrochemical oxidation of $(\text{SnCl})_{\text{ads}}$ to SnCl^+ (Step 2):



The Temkin isotherm conditions are applicable, i.e. the degree of coverage of the surface by $(\text{SnCl})_{\text{ads}}$, θ is $0.1 < \theta < 0.9$, while θ changes with the applied potential.

3.2. Region II

The Tafel region always extends to -0.5 V (E_L) in 0.5 and 1 M NaCl solutions over the entire range of temperatures investigated, whereas in 0.1 M NaCl solution, E_L shifts towards more negative potential values. The Tafel region is followed by a broad oxidation peak (region II, Fig. 1) associated with the formation of a white oxidation product on the electrode surface. The SEM pictures in Figs. 3 and 4 show the influence of the temperature (40 and 80°C) on the surface of a tin electrode in 1 M NaCl solution after an anodic polarization at 10 mV s^{-1} from -0.8 V to different potential limits. At 40°C, the surface is covered by a precipitate which increases in quantity as the potential becomes more anodic, as illustrated in Fig. 3. The potential limit is -0.3 V for Fig. 3a (at peak current on the voltammetric curve in Fig. 1); $+0.2\text{ V}$ for Fig. 3b (at the minimum on the voltammetric curve in Fig. 1); and $+1.3\text{ V}$ for Fig. 3c. At 80°C, however, only the surface roughness of the electrode increases and traces of precipitate are present (Fig. 4).

The strong influence of the temperature and time on

the dissolution of tin in 0.1 M NaCl solutions is illustrated in Fig. 5, where the anodic current is expressed against time at -450 mV for 25, 60 and 80°C. The low constant current suggests the formation of a passivating film on the electrode surface. At 25°C the shape of the $i-t$ transient is consistent with the case of the random precipitation. At 80 and 60°C the current passes through a maximum indicating that nucleation of a new phase and the growth process of a new passivating layer is involved. The SEM analysis shows that at 25°C the surface is covered by a thick white film (Fig. 6) while at 80°C the entire surface is covered by a black film (Fig. 7). The Auger spectroscopy analysis for the black layer suggests the formation of a tin oxide, while the white film at 25°C consist, most probably of $\text{SnOHCl}\cdot\text{xH}_2\text{O}$ (4).

3.3. Region III

In 1 M NaCl solutions at potentials more positive than 0.5 V a broad semi-passive current plateau exists at

Table 1. Effect of temperature on the behaviour of tin electrode in NaCl solutions at pH4

Temperature	25°C	40°C	60°C	80°C
1. Corrosion potential (mV)				
0.1 M NaCl	-588	-603	-616	-626
0.5 M NaCl	-606	-617	-630	-640
1 M NaCl	-620	-636	-654	-664
2. Tafel slope (mV dec^{-1})				
0.1 M NaCl	41.6	43.9	44.0	46.2
0.5 M NaCl	39.5	41.5	41.7	41.9
1 M NaCl	39.2	46.2	45.7	47.3
3. Order of reaction with respect to Cl^-	1.1	1.2	1.1	1.1
4. Corrosion current ($\mu\text{A cm}^{-2}$)				
0.1 M NaCl	1.7	2.6	2.7	3.4
0.5 M NaCl	1.7	3.1	2.7	3.5
1 M NaCl	1.5	4.1	3.9	4.5

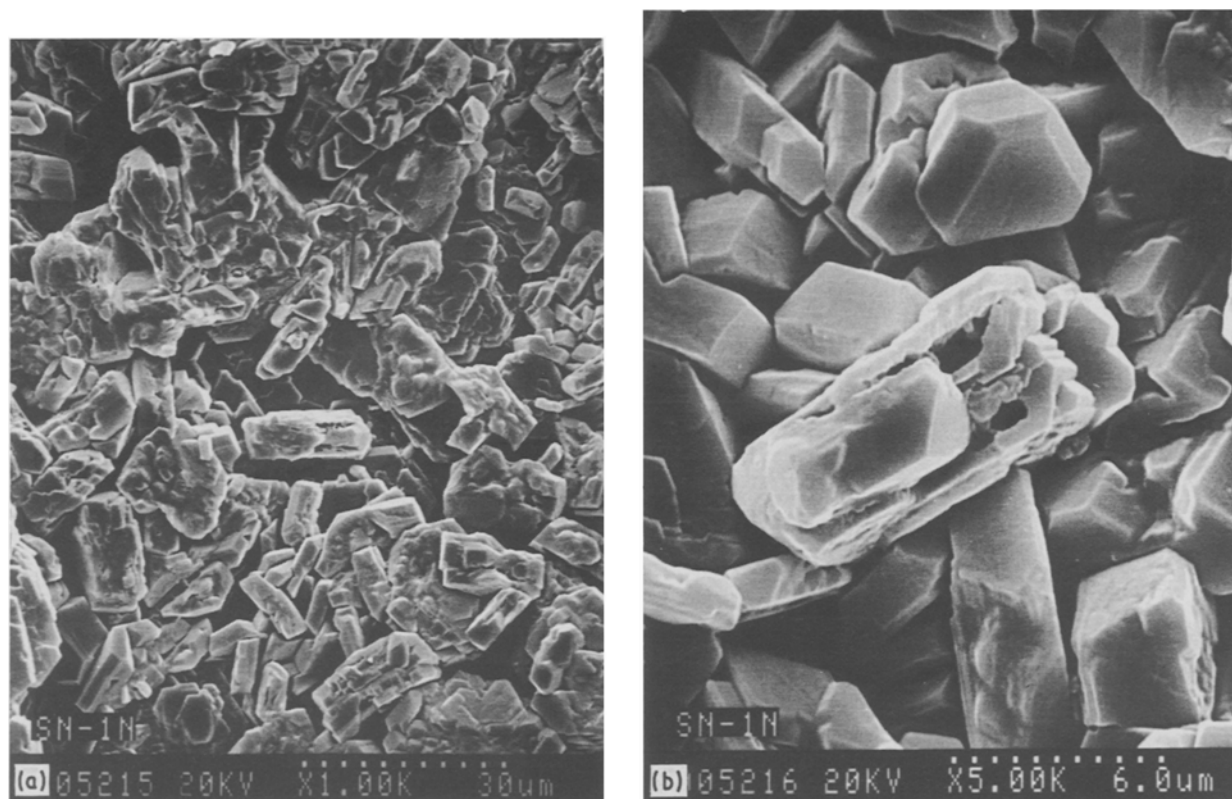


Fig. 8. SEM pictures of the tin electrode surface in 1 M NaCl solution at 25°C after anodic polarization at 10 mV s⁻¹ from -0.8 V to +1.3 V; magnification: (a) 1000× and (b) 5000×.

25°C, but decreases in length with increasing temperature. Subsequently, at 80°C, the semi-passive zone disappears and the current increases monotonically as the potential varies in the anodic direction; the current density becomes very high, reaching values in excess of 1 A cm⁻² at +1 V. The SEM pictures in Fig. 8 show the angular shape of the corrosion product at 25°C, characteristic of a dissolution-precipitation process, while at 40°C the corrosion product forms a relatively smooth film containing few cracks (Fig. 3c).

Practically no precipitates form at 80°C (Fig. 4b) but the surface becomes very rough. Furthermore, different amounts of chloride on the surface were found by EDX analysis: 54 atomic % at 25°C; 25 atomic % at 40°C and 10 atomic % at 80°C. These results indicate that with an increase in temperature from 25 to 80°C, the tin dissolution rate increases and the surface loses most of its passivity. In this region, the rate-determining step of tin oxidation is most likely the diffusion of an ionic species into the solution [4]. The formation of tin (IV) is possible and thermodynamically confirmed [5, 6].

4. Conclusion

The corrosion current of tin (at E_{cor}) is slightly dependent on temperature from 25 to 80°C and NaCl concentration from 0.1 to 1 M. The rate of anodic dissolution of tin, provided the electrode surface is bare, increases from 25 to 80°C, and with the Cl⁻ ion

concentration; the dissolution process remains the same.

If the potential is sufficiently anodic, the anodic dissolution no longer displays Tafel behaviour and the surface becomes partially, or entirely, covered with a corrosion product at or below 60°C. The morphology and nature of the corrosion products are strongly dependent on the temperature, Cl⁻ ion concentration, the applied potential and time of polarization. At high temperature (80°C) tin is passivated in low concentration (0.1 M) of chloride solutions, but as the concentration of Cl⁻ ions rises the passivity of the surface is not realized.

Acknowledgement

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