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Influence of sulphide ions on the cathodic behaviour of copper in 0.1 M borax solution

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The presence of sulphide ions in solution greatly influences the cathodic behaviour of copper in borax solutions (pH 9.2), even when this contaminant is in low concentration. Cyclic voltammograms, polarisation curves and Tafel plots are compared for polluted and unpolluted solutions. Prereduced and aged copper electrodes are investigated. The presence of sulphide ions in solution increases the rate of oxygen reduction on copper, thus having a detrimental effect on the global corrosion process. The transformation of the surface film into one with better conductive properties is suggested.

Keywords: *copper*, *corrosion*, *oxygen reduction*, *sulphide ions*

1. Introduction

Sulphide-polluted waters have a detrimental effect on the corrosion behaviour of copper-base alloys [1–9]. Most studies have been conducted in contact with seawater, some on copper-nickel alloys [2–10] and a few on bronzes and brasses [7, 8], because these materials are extensively used in marine environments. Seawater is frequently contaminated with sulphide from microorganisms, waste waters, rotting vegetation etc.

It has been established that the simultaneous presence of oxygen and sulphide causes accelerated attack [5]. However, although the mechanism of the oxygen reduction on copper has been studied [11], the role of sulphide on the electrocatalysis of the cathodic branch is still unclear.

To disclose the effect of other variables on the system (like alloying elements and/or other aggressive ions in solution) we chose to study the influence of sulphide ions on the kinetics of oxygen reduction on pure copper in 0.1 M borax solution (pH 9.2). In this condition, the solubility of copper oxides is very low and the nature and properties of these oxides has been thoroughly studied by Strehblow and coworkers [12–15].

2. Experimental details

The experimental set-up was described earlier [10]. Potentials were measured and are quoted with respect to a $Hg/Hg_2SO_4/K_2SO_4$ saturated reference electrode ($E = 0.64$ V vs NHE). Rotating-disc copper electrodes were machined from 99.99% copper (Metal Samples Co. Inc.) and inserted into suitable PTFE holders. A disc of 0.6 cm diameter (0.283 cm^2 area) was exposed. The electrodes were first abraded with emery paper and then mirror polished with 0.3 μm alumina. 0.1 M solutions of $Na_2B_4O_7.10\,H_2O$ approx. 99% were used as electrolyte. 2 and 10 ppm Na_2S were added from a stock saturated Na_2S p.a. solution, when indicated. All experiments were carried out at room temperature (18 ± 1 °C).

In the rotating disc experiments, a custom-built RDE was employed. A scanning potentiostat (EG&G model 362) was used to control current and potential. The polarization curves were recorded either potentiostatically or potentiodynamically. In the first case, the potential was varied in steps of 0.05 V, waiting at each potential until the current attained a stable value (typically about 1 min or less). This represents a steady-state situation. The current was recorded at each rotation rate (varying from 1.8 to 20 Hz) before switching to the next potential value. When the potentiodynamic curves were recorded, a triangular wave with a slope of 0.05 $V s^{-1}$ was used to represent an instantaneous behaviour. Those electrodes, referred to as 'prereduced', were held at -1.4 V in deaerated 0.1 M borax for 15 min, so as to obtain a standard starting condition for polished samples.

To guarantee a constant sulphide concentration throughout each of the experiments (preventing extensive sulphide oxidation by oxygen), air saturated solutions were preferred to oxygen saturated ones. In aerated 0.1 M borax solutions the oxygen concentration reaches 2.8×10^{-4} M, as measured with an oxygen sensor (Orion Research Inc.). The half-life of sulphide ions is about 30 min. The diffusion coefficient of oxygen was taken as $1.9 \times 10^{-5}\,cm^2\,s^{-1}$ [16].

The reflectance spectra of the copper electrodes were recorded using a commercial double-beam spectrophotometer, modified as described elsewhere [17]. The baseline corresponds to a copper electrode held at -1.4 V in deareated unpolluted electrolyte and was stored in the memory of the spectrophotometer.

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This spectral reflectance baseline R_0 was subtracted from each of the following spectra to calculate the changes in reflectance from the transmittance T, that is $(1-T)\% = 100\times(R-R_0)$, as a function of wavelength.

3. Results and discussion

3.1. *Prereduced (polished) electrodes in deaerated 0.1 M borax*

Figure 1 presents the effect of sulphide ions on the current–voltage behaviour of copper in deaerated 0.1 M borax solutions. The potential range is restricted to that of interest to the oxygen reduction. In unpolluted borax the current remains close to zero, except for a slight increase at the most negative potentials due to hydrogen evolution. Even at sulphide ion concentrations as low as 10 ppm, the effect on the magnitude of the cathodic current is strong. In the presence of sulphide ions, the negative-going scan shows a sharp peak at −1.48 V. Also, on the reverse scan, positive (anodic) currents are registered for potentials positive to −1.25 V.

It is difficult to identify positively and unambiguously the cathodic peak obtained in the presence of sulphide ions in the electrolyte. It is well-known that these ions can be oxidised to numerous compounds in aqueous solution, within an extensive range of oxidation numbers. For example, Syrett and coworkers [4] show that polysulphides and elemental sulphur interact with copper–nickel alloys producing a thick black scale rich in cuprous sulphide.

The reduction of sulphur may be described as

$$S + H_2O + 2\,e^- \rightarrow HS^- + HO^- \qquad (1)$$

where, considering $E^\circ = -0.478$ V vs NHE, $[HO^-] = 1.6\times10^{-5}$ M and $[S^{2-}] = 3.4\times10^{-4}$ M, we can use the Nernst equation to calculate the reversible potential for the present reaction in our experimental conditions. This correction results in $E = -0.98$ V vs Hg/Hg_2SO_4, far from the potential of the peak observed (see Fig. 1).

Another possibility is the reduction of Cu_2S. The potential against pH plot (Pourbaix diagram) for the Cu–S–O–H system [18] shows Cu_2S as a stable phase at pH > 9, and at potential values negative to the Cu stability area. For the reaction

$$Cu_2S + H_2O + 2\,e^- \rightarrow 2\,Cu + HS^- + HO^- \qquad (2)$$

$\Delta G^\circ = 179.66$ kJ. Thus, we can calculate $E^\circ = -0.931$ V versus NHE, which, applying the Nernst equation to our experimental conditions, results in $E = -1.432$ V versus Hg/Hg_2SO_4, in good agreement with the potential of the peak shown in Fig. 1.

Spectroscopic evidence for this second option is presented in Fig. 2. Differential reflectograms were recorded in sulphide-contaminated deaerated 0.1 M borax at various characteristic potentials within the range investigated in Fig. 1. As seen in Fig. 2, a film develops on the electrode as the potential is fixed at various values positive to −1.3 V. This corresponds to the appearance of positive currents in the voltammogram of Fig. 1. The shape of the spectra does not correspond to either Cu_2O or CuO [11, 17], so it is possible that the reverse of Reaction 2 is taking

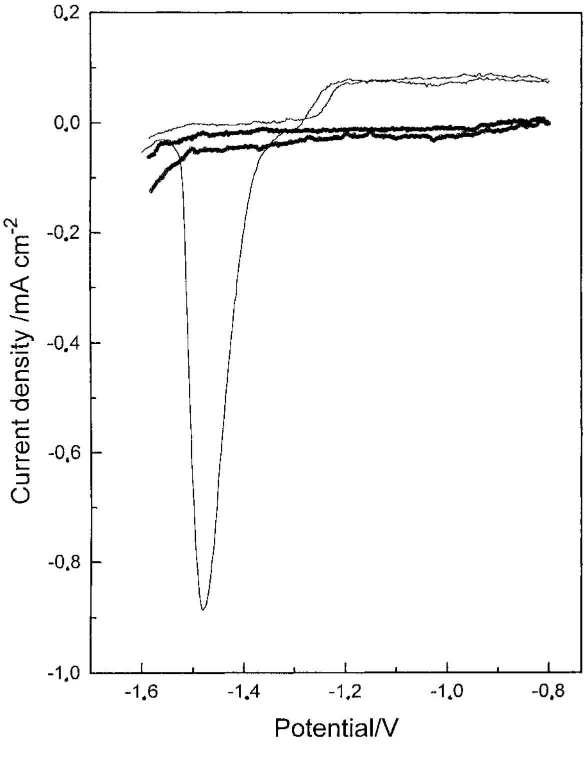

Fig. 1. Current–potential curves for Cu in contact with deaerated 0.1 M borax solution. Scan rate 0.02 V s^{-1}; rotation rate 6.4 s^{-1}. Key: (——) sulphide-free solution; (——) when 10 ppm S^{2-} are added.

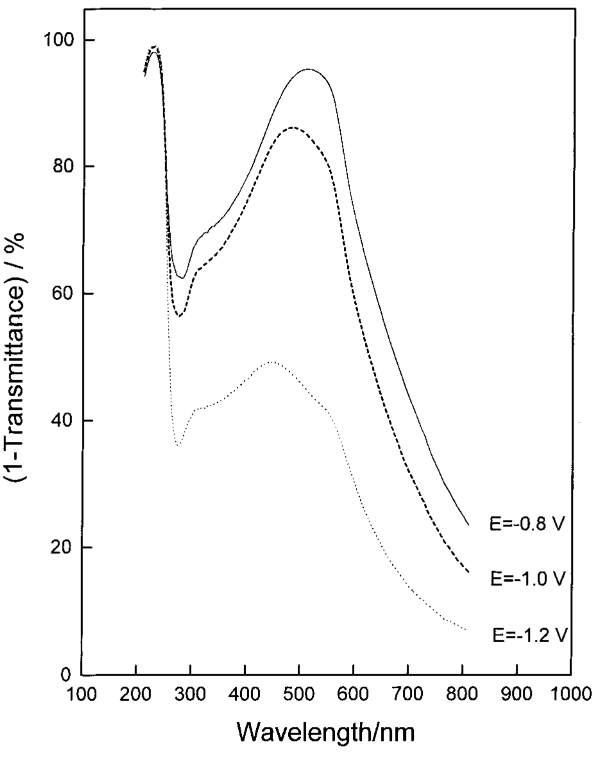

Fig. 2. Differential reflectance spectra for copper in deaerated 0.1 M borax contaminated with 2 ppm S^{2-}. Electrode is successively held 10 min at each potential shown, before recording the spectrum.

place. The peak at 250 nm results from the presence of sulphide ions in solution and corresponds exactly to standard u.v. spectra of sulphide-contaminated borax solution.

3.2. *Prereduced (polished) electrodes in aerated 0.1 M borax*

The influence of the simultaneous presence of dissolved oxygen in solution was then investigated. In Fig. 3, cathodic polarisation curves with and without sulphide ions are superimposed for comparison. For each condition, the results for both potentiodynamic and potentiostatic potential sweeps are presented. When polished copper is in contact with sulphide-polluted 0.1 M borax solution, its rest potential shifts about 0.17 V in the negative direction (from about −0.5 to −0.67 V). Other authors [1, 5, 9, 10] have observed this same effect for copper alloys in various electrolytes. Because of this shift, the current approaches zero at much more negative potentials, and so the potential range under investigation has to be restricted when sulphide ions are present in solution, in order to avoid undesired influence of the anodic branch. The limiting current decreases slightly in the presence of sulphide, probably because the oxygen concentration decreases as part of the oxygen is consumed in oxidizing the sulphide ions.

The data presented in Fig. 3 can be plotted as current density vs. the square root of the rotation rate (Levich plot) within the purely diffusional range and also as the inverse of the current density against the inverse of the square root of the rotation rate (Koutecky–Levich plot). In sulphide-free solution, the number of electrons taking part in the cathodic half-reaction can be calculated as 3.8. Assuming that a low S^{2-} concentration produces no salting-out effect on the oxygen (O_2) concentration and that all the other parameters involved remain constant, it can be calculated that the oxygen concentration drops some 13% due to chemical reaction between oxygen and sulphide ions.

Oxygen reduction on copper in aerated 0.1 M borax gives Tafel slopes around −0.2 V dec^{-1}. However, when sulphide ions are present in the electrolyte the Tafel constant drops to −0.12 V dec^{-1} (see Fig. 4). Tafel slopes higher (in absolute value) than the expected −0.12 V dec^{-1} were explained earlier as due to the presence of a duplex passive film composed of Cu_2O/CuO and present on the electrode surface even at very negative potentials [11, 19]. The chemical nature of the passive film is clearly different when sulphide ions are present in the electrolyte. The incorporation of sulphide ions into the film probably improves the electronic conductivity [4], this effect being, in turn, reflected in smaller values of the Tafel slope.

In unpolluted deaerated 0.1 M borax solution, the passive film on copper is mainly composed of cuprous oxide [11, 17]. In aerated solutions part of the Cu_2O is transformed into CuO, so that a duplex film Cu_2O/ CuO is always present on the metallic surface. When aerated solutions are further polluted with sulphide ions, Cu_2O can also be transformed into Cu_2S, as described by:

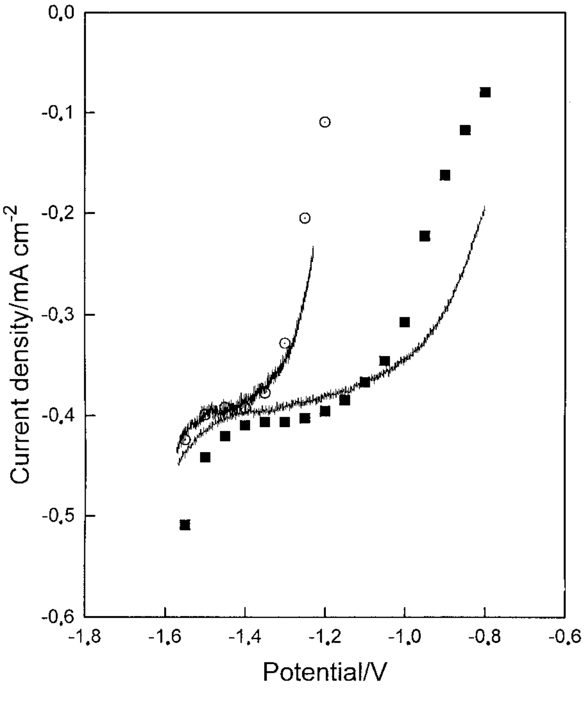

Fig. 3. Current–potential curves for Cu in contact with air-saturated 0.1 M borax solution. Potential is stepped starting from −1.6 V. Full line below each represents same condition, but potential is swept at 0.05 V s^{-1}. Rotation rate 6.4 s^{-1}. Key: (○) 0.1 M borax + 10 ppm S^{2-}; (■) sulphide-free 0.1 M borax.

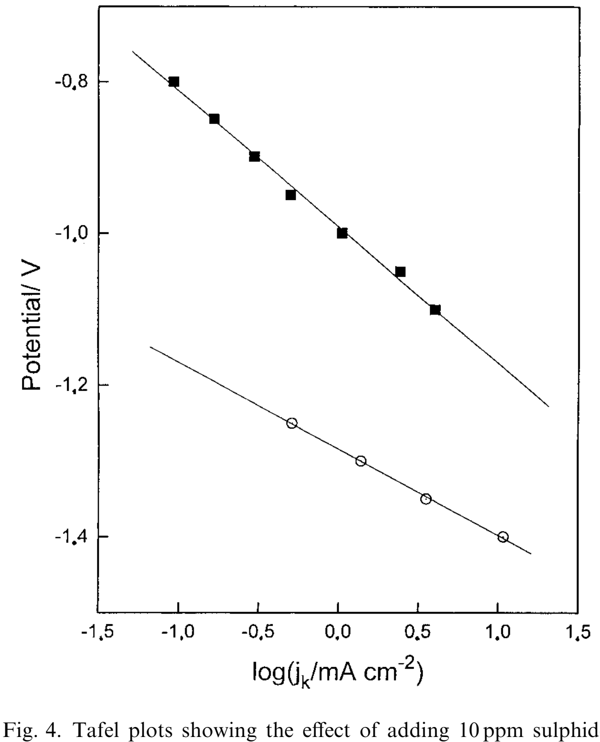

Fig. 4. Tafel plots showing the effect of adding 10 ppm sulphide ions. Key: (○) 0.1 M borax + 10 ppm S^{2-}; (■) sulphide-free 0.1 M borax.

$$Cu_2O + HS^- \rightarrow Cu_2S + HO^-$$

$$K_{eq} = 1.07 \times 10^{18} \qquad (3)$$

Figure 5 shows spectroscopic evidence for the modification of the Cu_2O film when first O_2 and then S^{2-} are present in the electrolyte.

Figure 5(a) shows the spectrum of the film present on a copper surface after keeping the electrode at rest potential in contact with deaerated unpolluted 0.1 M borax solution for 10 min. After bubbling oxygen for 15 min CuO grows on the Cu/Cu_2O substrate, as seen by the relative increase in the signal within the u.v. range (see Figure 5(b)) [17]. 2 ppm S^{2-} were added to the same solution and the spectrum shown in Figure 5(c) was recorded after 15 min. This latter spectrum may be attributed to Cu_2S formation on an oxidized $Cu/Cu_2O/CuO$ substrate. This film appears to be thicker but is probably more porous, as suggested by other authors [4]. The shape of spectrum 5(c) is equivalent to that resulting from adding spectrum 5(b) plus any of the spectra in Fig. 2.

The spectra in Fig. 5 reflect changes occurring on a copper specimen after forming Cu_2O at open circuit potential. However, this interpretation for Cu_2S formation would also apply for prereduced copper electrodes. Evidence for the presence of a thin Cu_2O layer on a Cu electrode held at relatively negative potentials, even negative to the main Cu_2O reduction peak wave in a cyclic voltammogram, were given previously [19–21].

3.3. *Aged electrodes*

The results described above show the effect of sulphide ions on freshly polished electrodes. In spite of being a necessary reference, these are far from representing real conditions for corrodible metals such as copper and its alloys. Attention is now turned to the investigation of 'aged' electrodes, i.e. electrodes left immersed in either polluted or sulphide-free solution at open-circuit potential for 30 min before electrochemical testing. This ageing time was chosen taking into account the life-time of sulphide ions in aerated solutions. After this pretreatment, the potential sweep was initiated from the most positive end and proceeded in the negative direction.

The effect of ageing on the polarization curves recorded in unpolluted solution is presented in Fig. 6. The potential scan starts from −0.8 V. The results obtained by means of two experimental techniques appear superimposed. When the curves are registered potentiodynamically, the current in the polarization curves results from the addition of two processes: the reduction of the film grown during the ageing stage and oxygen reduction. The corresponding peak can be observed at −1.08 V, in good agreement with the position of the cuprous oxide reduction peak in the cyclic voltammograms [11]. There is also a shoulder at −1.28 V which can be attributed to cupric oxide reduction. In the reverse scan, after the oxides have been reduced, the current in the activated region is higher. This shows a well-known effect: passive films

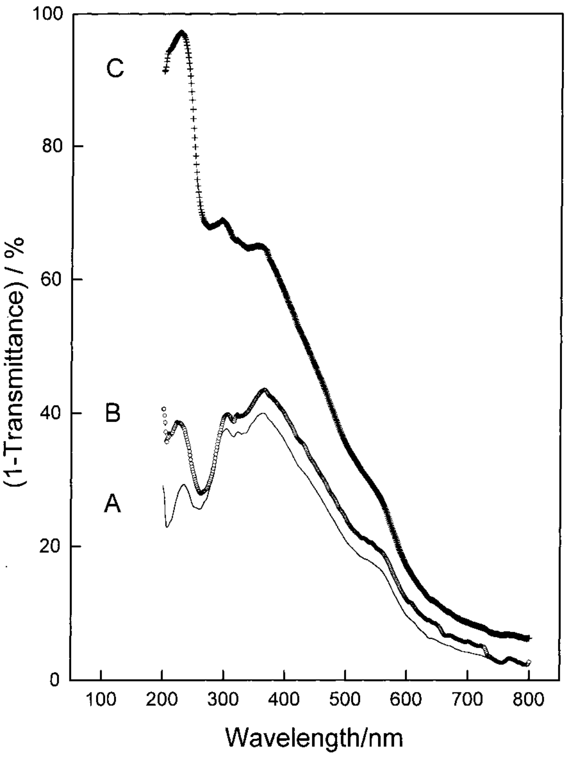

Fig. 5. Differential reflectance spectra for copper: (a) Cu_2O, 5 min at open circuit potential in deaerated 0.1 M borax solution; (b) 15 min after saturating former with oxygen; (c) 10 min after 10 ppm S^{2-} are added to the oxygenated solution.

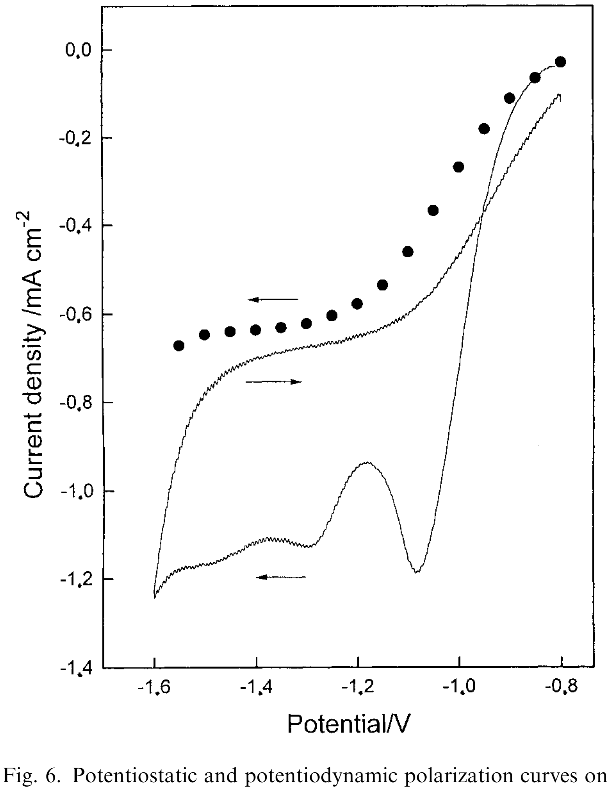

Fig. 6. Potentiostatic and potentiodynamic polarization curves on Cu aged for 30 min in 0.1 M borax at open-circuit potential. Rotation rate $10.4\,s^{-1}$.

on copper inhibit oxygen reduction (the reaction rate decreases) [11]. For this same reason, when the curves are registered potentiostatically, the current remains lower than that obtained for polished copper in the activated range.

When 10 ppm sulphide are added while the polarization curve is being recorded, but not during the ageing period, the resulting curves are quite different (Fig. 7). The potential is scanned from −0.8 to −1.6 V. Again, two experimental procedures are compared. When the potential is continuously swept a cathodic peak appears that can be attributed to Cu_2S reduction (compare to Fig. 1). This shows that the incorporation of sulphide into the film is fast, because the potential scan is initiated immediately after immersion in the contaminated solution. In this case, and in contrast with the results presented in Fig. 6, the current in the activated region (namely, from −0.8 to −1.0 V) is higher in the forward sweep. Thus, the sulphide-modified film activates and accelerates the oxygen reduction and the current in the reverse sweep decreases after the film is reduced. When the potential is stepped, the current increases steadily and no limiting current is evident. High currents, typical of hydrogen evolution, are also detected at potentials much less negative than in the absence of sulphide in solution (compare to Fig. 6).

Finally, the effect of the presence of sulphide ions during the ageing period was investigated. In this case, the electrode was held for 30 min at rest potential in aerated 0.1 M borax containing 10 ppm S^{2-}. The electrodes were then rinsed and immersed in aerated sulphide-free 0.1 M borax solution. Potentiostatic and potentiodynamic scans were performed between −1.2 and −1.6 V and the corresponding results are compared in Fig. 8. When the potential is swept, a peak again appears in a position close to that shown in Fig. 1. The current increase due to hydrogen evolution is again observed at less negative potentials. In the reverse sweep, after oxide reduction, the current decreases but remains higher than in any of the other reported conditions. This is probably because a thicker Cu_2S film forms under the present condition. The potentiostatic curve also shows the highest current values. Clearly, this is the worst ageing condition.

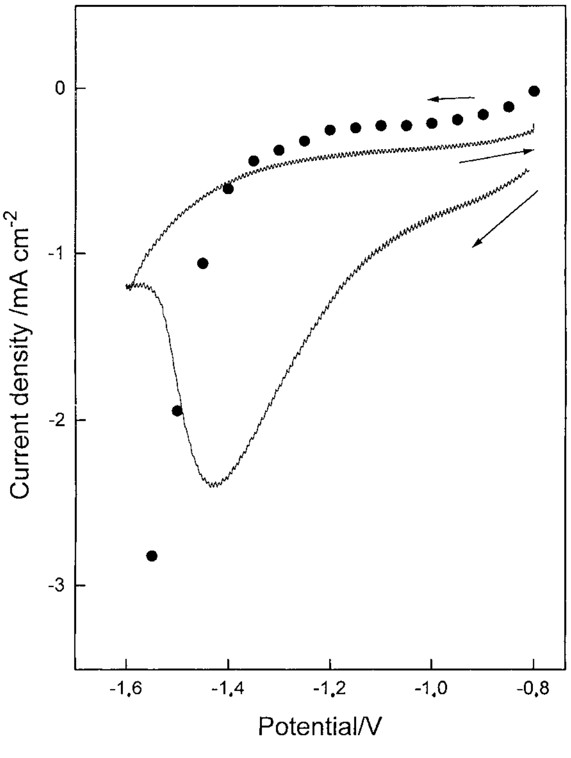

Fig. 7. Potentiostatic and potentiodynamic polarization curves recorded on 10 ppm sulphide-polluted 0.1 M borax for Cu aged for 30 min in 0.1 M borax at open-circuit potential. Rotation rate 10.4 s^{-1}.

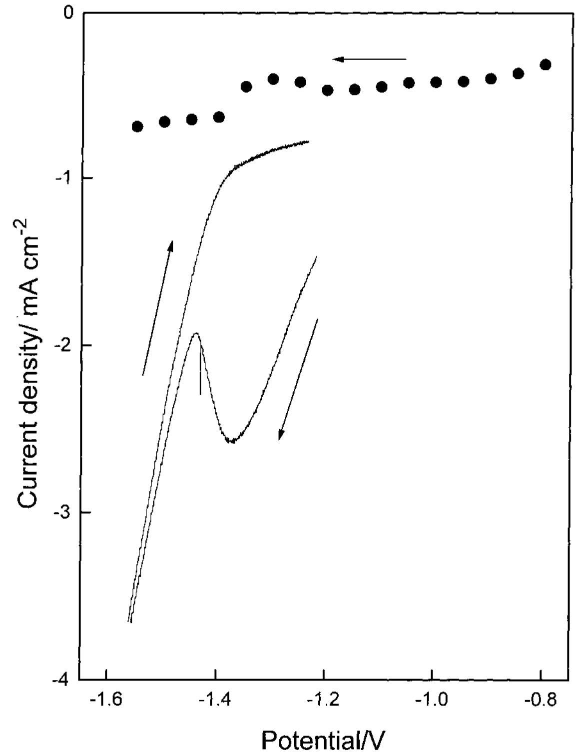

Fig. 8. Potentiostatic and potentiodynamic polarization curves recorded on 0.1 M borax for Cu aged for 30 min in 10 ppm sulphide-polluted 0.1 M borax at open-circuit potential. Rotation rate 10.4 s^{-1}.

The whole set of results indicates that the presence of sulphide is always detrimental, being even worse when it can incorporate into the passive film during the ageing stage. One reason for this may just be that sulphide ions, copper and cuprous oxide have more time to interact. However, it also shows that the effect persists even after the sulphide ions have been removed from the solution, suggesting a modification of the passive film composition and/or structure.

4. Conclusions

The following remarks can now be made:

(i) Even in very low concentration, sulphide ions are able to modify the rate and potential range where oxygen reduction takes place in 0.1 M borax.

(ii) Tafel slopes are greatly reduced when 10 ppm sulphide is present in solution, suggesting an improvement in the conducting properties of the passive films.

(iii) The nature of the surface film changes in the presence of sulphide, as evidenced by both polarization curves and reflectance experiments.

(iv) The presence of sulphide in solution always increases the rate of oxygen reduction on copper, thus having a detrimental effect on the global corrosion process. The effect is larger when the electrodes are aged and sulphide is present during the ageing stage.

(v) The behaviour of the system is highly dependent on the exposure conditions of the copper specimen, so that the results are difficult to compare with those obtained by other authors.

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