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CHARACTERISATION OF PASSIVE FILMS ON COPPER AND BRASS BY PHOTOELECTROCHEMICAL TECHNIQUES*

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Photopotential, interfacial capacitance and absorption spectra of passive films on copper and brass were measured in order to understand their semiconducting properties. On the addition of inhibitors such as benzotriazole and ferrous sulphate, the films become more insulating and on the addition of chloride ions the films ruptured.

Keywordscopper, brass, passive films, photoelectrochemical techniques

INTRODUCTION

Measurement of photocurrent and photopotential has become an important tool in the investigation of the electrical properties of passive film. Knowledge about the semiconducting properties like band gap, conductivity type and flat band potential plays a major role in understanding the metal/metal oxide/electrolyte interfaces. The composition and structure of passive films can be determined by various surface analytical techniques like AES, ESCA and electron microprobe analysis. However, significant changes in structure and composition an occur before such measurements are made; in situ techniques like ellipsometry, reflectance spectroscopy and internal reflectance spectroscopy can provide information on the qualitative nature of the passive films and nothing about their electronic properties. The electrochemical properties of the passive films on metals/alloys can be interpreted in terms of semiconducting properties of the films and suitable relationship can also be formulated between the type of conductivity and the protection efficiency of the passive films. In recent times, much attention has been focused on characterising the electronic properties of the passive films formed on the metals and alloys by photoelectrochemical techniques [1 to 5].

While interfacial capacitance measurements on passive films can provide information on the electronic structure of an oxide film, photoelectrochemical methods can give one an idea of the conductivity type of the film and composition of the film. Most of the theories of passive film characterisation by photoelectrochemical methods are based on the assumption that the film's behaviour is very much like that of a solid state semiconductor. Normally, on illumination the structure of the oxide film is very much altered by the formation/separation of electron-hole pairs, resulting in a nonuniform doping within the oxide film. If the metal/metal oxide/electrolyte interface is illuminated by a light having an energy hν, electrons can be excited from occupied to unoccupied states within the electrode, as:

$$h\nu \longrightarrow e^- + h^+ \qquad (1)$$

The electron-hole pair formation according to the above expression is the basic reaction for photoelectrochemical effects [6]. These effects are often reflected as changes in the measured current/potential. Depending upon the properties of the passive films the observed changes in potential or current will help in classifying them as p-type or n-type or insulating type and also in determining other electrical parameters. The electronic properties evaluated by such measurements contribute significantly to the understanding of the kinetics of the corrosion and film formation process.

In this investigation, attempts have been made to characterise the passive films formed on copper and brass surfaces in weak, aerated alkaline solution and also to examine the effect of chloride ions and inhibitors on the film formation process.

EXPERIMENTAL

Two identical electrodes of high purity, polished to a mirror finish, degreased with trichloroethylene and lacquered to get a geometrical area of 0.5 cm^2, were exposed to the medium (0.1M NaOH). A cell made of PVC, consisting of two compartments separated by a thin perforated PVC sheet, was so designed that one electrode could always be kept in dark in one compartment while the other could be irradiated through a quartz window.

A high power Hg-Xe light source was used to illuminate the electrode surface. Interference filters of wavelength 400, 435.4, 500, 550, 600 and 650 nm were also employed for measuring the photopotentials at various wavelengths. Solutions of AR grade sodium hydroxide, sodium chloride, benzotriazole (BTA), mercaptobenzotriazole (MBTA) and ferrous sulphate ($FeSO_4$) in triple distilled water were used. The potential difference between the two electrodes were continuously monitored using a programmable multivoltmeter and the photopotentials were measured for every hour (the term photopotential refers to the potential difference between the illuminated electrode and the other in the dark).

The capacitance measurements were carried out with the conventional three electrode cell using PAR Electrochemical Impedance System. A double beam UV 3400 spectrophotometer (Hitachi, Japan) was used to obtain absorption spectra of oxide films. The electrochemical noise was measured with a signal processor (Solatron 1200, UK) [7].

RESULTS AND DISCUSSIONS

COPPER

The properties of the passive films on copper have been discussed for a long time, but as yet there is no clear understanding of their properties, structure etc. Normally copper forms passive films in weak, aerated acidic and alkaline solutions [8]. Detailed electrochemical and surface analytical studies indicate that the passive films formed on copper appear to consist of Cu_2O or a mixture Cu_2O and CuO or $Cu(OH)_2$ [9 to 11]. Not much attention has been given to understand the electronic properties of the passive films or to the participation of these semiconducting oxides in corrosion reactions.

(i) Photopotential measurements: The positive photopotentials (Fig. 1) observed for the passive film on copper in 0.1M NaOH after various intervals of time suggest the formation of p-type oxide film. This is due to the increasing positive charge at the metal/electrolyte interface. Passivation of copper in alkaline medium occurs through two stages, viz. formation of Cu_2O and CuO. The film initially consists of Cu_2O and shows the characteristics of a p-type semiconductor. The origin of this positive photopotential may be explained as follows:

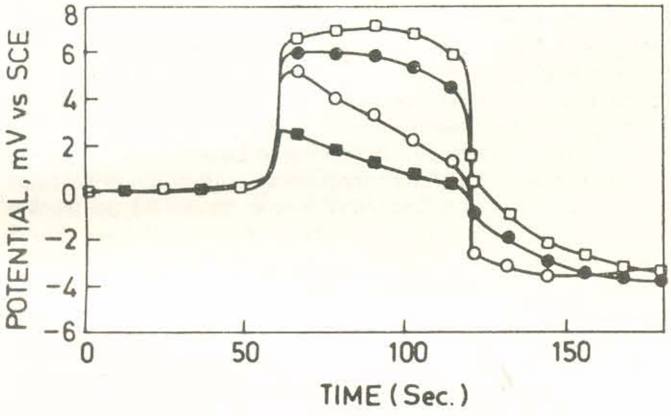

Fig. 1: Photopotential of copper in 0.1M NaOH as a function of durations of immersion. -●-*15 min;* -+-*60 min;* -∗-*120 min;*-□-*190 min.*

Illumination of the passive film from the solution side creates electrons and holes in the Debye region of the oxide film. The electrons move towards the oxide/solution interface and take part in the reduction of oxidants in solution while holes move towards the bulk of the metal because of the depletion nature of the space charge layer [12]. This increase in occupancy of electrons in the depletion layer causes the shifting of the Fermi level in the negative direction with respect to the electrode kept in dark. This negative shift in Fermi level gives rise to the potential shift of the illuminated electrode in the positive direction as the energy and potential scales are related by

$$V = q\,(-4.5\text{ eV} - E) \qquad (2)$$

where q is the electronic charge.

As soon as the light is cut off, the observed potential difference falls much below the initial value due to the back reaction of the photogenerated species as suggested by Hardee and Bard [13]. Photogenerated species in this case may be due to the presence of dissolved oxygen or some intermediate compounds formed. According to Osche and Rosenfeld [14] the photopotential of metal oxide can be expressed as

$$V_{ph} = (KT/q)\ \ln\,(N_A/N_D) \qquad (3)$$

where N_A and N_D are the concentration of acceptor and donor defects respectively. All other symbols have their usual meaning. According to this expression the concentration of acceptor and donor correspond to those of excessive anion and cation to the stoichiometric composition of the oxide film. Hence eq. (3) suggests that the p-type semiconducting oxide film containing excessive anion (acceptor) shows a positive photopotential and vice versa. Hence the above results agree with Oshe and Rosenfeld model.

The variation of photopotential with time in the presence and absence of different concentrations of inhibitors is shown in Fig 2 and Fig. 3.

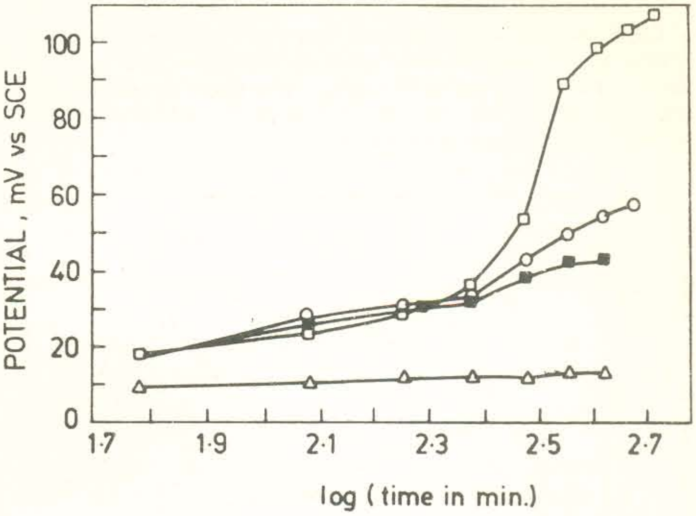

Fig. 2: Variation of photopotential for copper in 0.1M NaOH with the addition of BTA. □ *Blank;* † *B1 + 1 ppm;* ◇ *B1 + 5 ppm;* △ *B1 + 10 ppm.*

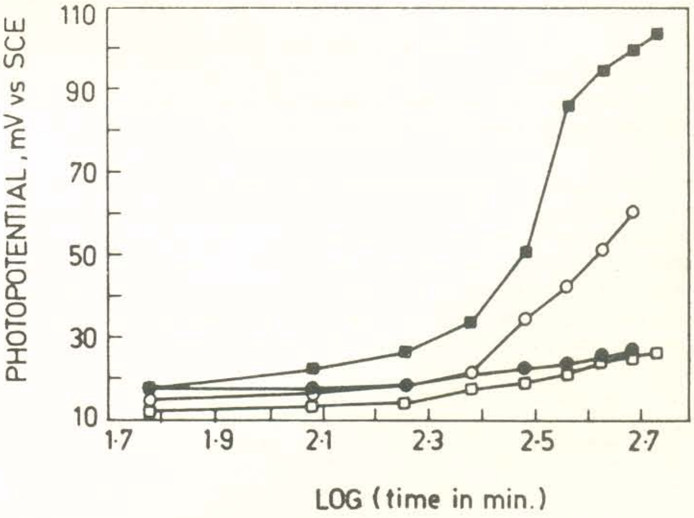

Fig. 3: Variation of photopotential for copper in 0.1M NaOH with the addition of $FeSO_4$. □ *Blank;* † *B1 + 1 ppm;* ◇ *B1 + 5 ppm;* △ *B1 + 10 ppm.*

The logarithmic increase of photopotential of copper in alkaline medium is also an indication of logarithmic growth of the film with respect to time, as reported in the case of iron [15]. At the end of the experiment, a thick, adherent and black film could be seen. However, the film growth is slowed down considerably, as expected, with the addition of inhibitors. As the concentration of the inhibitor exceeds a certain critical value, the change in photopotential becomes less or negligible in the case of BTA whereas the photopotential continues to increase, though slightly, in the case of ferrous sulphate. This indicates that the passive film formed in the presence of a higher concentration of BTA is not a simple oxide film. The visual observation indicates a partial coverage of the surface by the black film at lower concentrations of inhibitor. At higher concentrations of inhibitors, the metal is bright and without any black film.

Figure 4 shows the spectral distribution of photopotential in sodium hydroxide for various durations. Up to 5 hours, the photopotential peak centres around 500 nm, which is characteristic of Cu_2O. After 5 hours this peak disappears and two new peaks around 435 nm and 550 nm appear, indicating that with time, the film is a mixture of oxides of copper. This result agrees with the earlier observation [16], that the irradiation of Cu_2O promotes its own photo-reduction and oxidation.

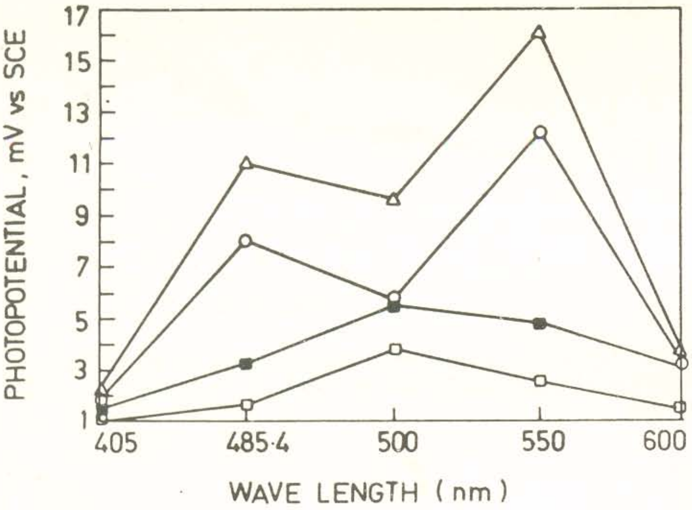

Fig. 4: Wavelength spectra of photopotential of copper in 0.1M NaOH after given immersion periods. □ *3 h;* † *5 h;* ⋄ *7 h;* △ *9 h.*

In indicates the photopotential spectrum in the presence of inhibitors (Fig. 5). Here it is seen that the photopotential peak around 500 nm continues to grow even after 5 hours indicating that addition of inhibitor restricts the formation of mixed oxides. The growth of Cu_2O with time is rather more in the presence of ferrous sulphate than in the presence of BTA. It is known that the passive film on copper consists of Cu_2O and inhibitor complexes [17].

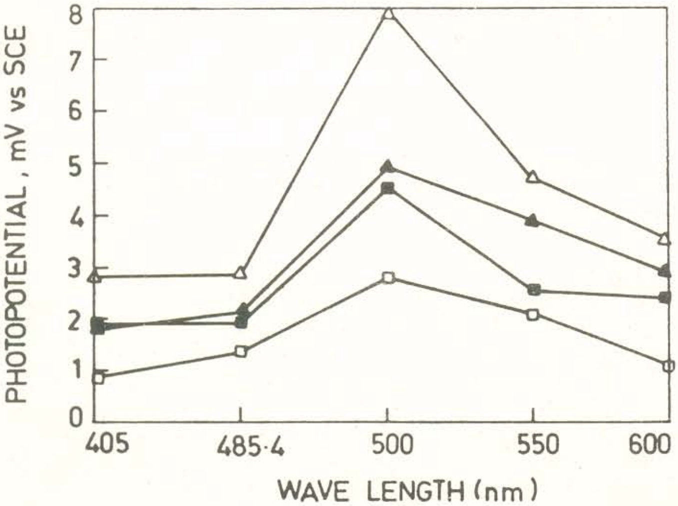

Fig. 5: Wavelength spectra of photopotential for copper in 0.1M NaOH with given inhibitor additions after given immersion periods. □ *5 ppm BTA, 5 h;* ⋄ *5 ppm $FeSO_4$, 5 h;* † *5 ppm BTA, 7 h;* △ *5 ppm $FeSO_4$, 7 h.*

(ii) Flat band potential measurements

One of the important methods of characterising the semiconductive behaviour of passive films is by the measurement of Flat Band potential. It is the potential at which the band edges do not bend. In other words, there will be no potential drop in the Debye region of oxide film. If flat band potential is known, the position of band edges on the electrochemical scale and the direction of band bending and in some special cases, the magnitude of band bending can be determined.

A simple and versatile method, among the various methods available for flat band potential measurement is the application of Mott-Schottky (MS) plot. In the case of the depletion layer, the inverse square of space charge capacitance is related to potential by Mott-Schottky relation,

$$C_{SC}^{-2} = \frac{2}{\epsilon\epsilon_0 q\, N_A}[V - V_{fb} - kT/q] \qquad (4)$$

Thus extrapolation of the linear region of the plot of $1/C^2$ vs V curve to potential axis will give flat band potential + KT/q (= 26 mV). The latter can frequently be ignored. The intercept of the potential axis directly gives the flat band potential.

MS plot of copper in 0.1M NaOH for three different frequencies are given in Fig. 6. The extrapolation of the linear region of the depletion layer intersects the potential axis at different potentials. The frequency dispersion observed in MS plot has been analysed by many authors [18 to 20]. According to Dutoit, if the set of MS plots are parallel for different frequencies with different potential intercepts then it is classified under A-type. In the B-type, the MS plots for different frequencies intersect the potential axis at the same point with different slopes. Hence one can get information regarding the carrier concentration from A-type and flat band potential from B-type. Since the flat band potential decides many factors of the semiconducting film, it is desirable that the behaviour of the system to be of B-type with minimum frequency dispersion. The set of MS plots shown in Fig. 6 is a combination of A and B - type. Similar results have also been obtained by Dipaulo for SS [21]. In such situations it is not possible to obtain the exact values of flat band potential for passive films formed on metal surfaces and hence it should be restricted to one frequency for studying the effect of roughness, pH and other factors.

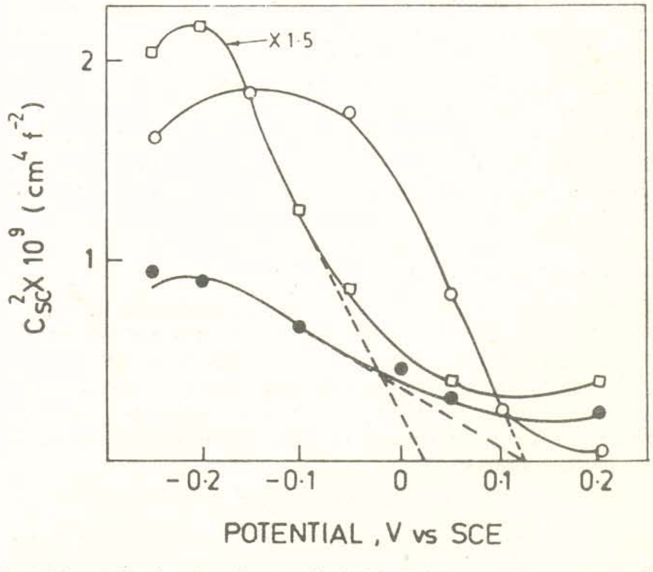

Fig. 6: Mott-Schottky plot of copper in 0.1M NaOH. ○ *10 Hz;* ● *100 Hz;* □ *1000 Hz.*

Table I shows the acceptor concentration (N_A), and flat band potential measured using Mott-schottky relation.

These results support the fact that addition of BTA inhibits film growth considerably when compared to ferrous sulphate. The presence of inhibitor shifts the flat band potential to the more positive direction, the shift being larger in the case of more effective inhibitor.

TABLE-I: Effect of inhibitor additions on flat band potential V_{fb} and acceptor concentration N_A for copper in 0.1M NaOH

Inhibitor addition, (ppm)	N_A (ml)	V_{fb} (V)
0	2.116×10^{21}	0.134
5 $FeSO_4$	9.406×10^{16}	0.204
5 BTA	3.762×10^{16}	0.254

Table II shows the measured V_{fb} and N_A of the passive films on copper. At all frequencies the shift in V_{fb} for a rough surface is in the cathodic direction when compared to mechanically polished electrodes, the shift being more at high frequency. The density of acceptor concentration increases with the roughness of the electrode surface for all the three frequencies. The shift in V_{fb} is similar to that observed for semiconductor electrode and is attributed to increase in the number of surface states on the electrode. In this case, the artificially altered nature of the surface leads to the formation of a thin amorphous layer of the passive film having a nonuniform distribution of carrier concentration and also the contribution of surface states to the capacitance leading to a A or B type behaviour of MS plots.

TABLE-II: Influence of surface roughness on V_{fb} and N_A

Freq. (Hz)	Mechanical polish to mirror finish		polished with 4/0 emery		polished with 2/0 emery	
	V_{fb} (V)	N_A (ml)	V_{fb} (V)	N_A (ml)	V_{fb} (V)	N_A (ml)
10	0.134	2.11	0.130	3.29	0.105	5.83
100	0.134	6.78	0.095	7.68	0.075	9.36
1000	0.024	0.13	−0.005	0.15	−0.052	2.77

(iii) Band gap measurements: Figure 7 shows the corrected absorption spectrum of passive film formed on copper in 0.1M NaOH for various time intervals. The absorption peak at 480 nm after 6 h is more pronounced than those obtained after one and three hours indicating the presence of stable cuprous oxide with a band gap of 2.13 eV.

(iv) Noise measurements: Table III gives the influence of irradiation on the auto power of noise spectrum (200 mHz - 10 Hz) for copper in 0.1M NaOH solution. These data show that in the dark, not only the noise power is low but also the changes are very small. On illumination, there is an increase of noise power with time. Generally, the film formed is very thin and amorphous in nature. Further, the growth of the film is enhanced by the transport of metal cations to the oxide/electrolyte interface through the defects in the oxide film. However in the dark the increase in the carrier concentration on the film is negligible even though the thickness of the film increases with time. On illumination, nonequilibrium electrons and holes are formed and the carrier concentration at the surface increases leading to the acceleration of the electrode reaction. As the film grows, it will absorb more light generating electron-hole pairs which lead to the increase in noise power.

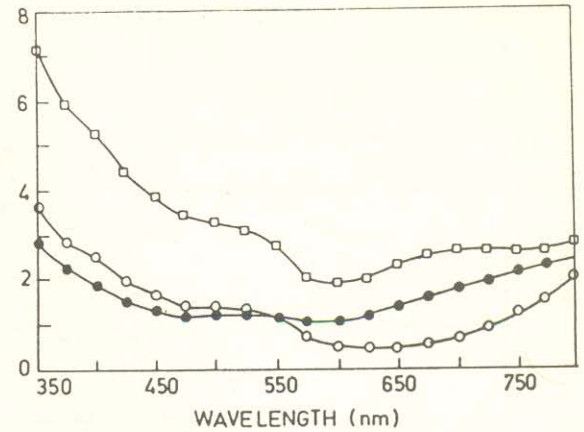

Fig. 7: Corrected absorption spectrum of passive film on copper in 0.1M NaOH. † 1 h; ◇ 3 h; □ 6 h.

TABLE-III: Noise Power of the Copper in 0.1M NaOH measured at different durations of time

Time (h)	Auto Power Dark	Auto Power Light
1	1.8726E-11	6.2132E-8
2	2.0736E-11	8.8921E-8
3	2.2009E-11	1.2805E-10
4	1.4915E-11	8.8278E-10
5	1.0959E-11	1.1641E-8
10	6.6937E-11	9.7231E-8
15	6.9848E-11	1.4041E-6

BRASS

Though the electrochemical and spectral properties of the passive film on brass have been examined in detail [22 to 24], there is not much information about their electrical properties. The electronic properties of the passive films on brass will also be of help in understanding such process better.

(i) Photopotential measurements: The photopotentials observed for brass in 0.1M NaOH is less than that of copper [25]. The oxides of zinc and copper differ as ZnO exhibits properties of n-type semiconductor while CuO or Cu_2O exhibits that of p-type. The increase in photopotential of the passive film on brass with time can be due to the enrichment of oxides of copper or some intermediate compounds formed because of the enrichment of copper on the surface.

Figure 8 shows a two step linear increase in photopotential as the film grows in the presence and absence of chloride ions. It has already been seen that the oxide film formed on copper initially consists of Cu_2O, and with time consisted of mixed oxides of copper like CuO/Cu_2O, $Cu(OH)_2$. Similar effect is observed in the case of brass also as the effect of zinc oxide is negligible. The thickening of the film is also confirmed by the increasing charge transfer resistance with time as shown by Nyquist plot (Fig. 9) of the complex impedance of brass in 0.1M NaOH system.

Increase in the photopotential with the addition of chloride ions in small concentration may be due to the accumulation of negative charges at the oxide/electrolyte interface. In other words, the thickness of the film increases upto a certain concentration of chloride ion addition. Also in these concentrations, presence of excess hydroxyl ions dominate the film formation process [26].

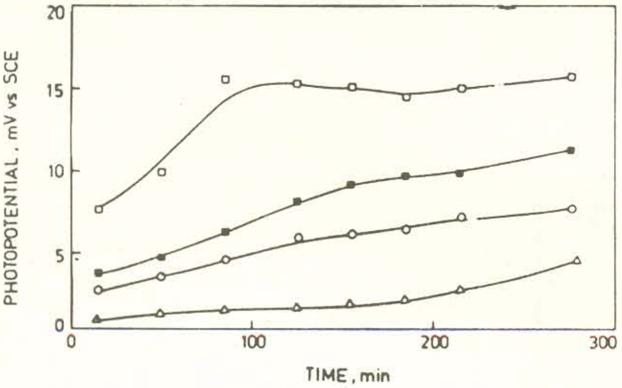

Fig. 8: Variation of photopotential for brass in 0.1M NaOH and the effect of chloride addition with time. ○ *Blank;* ■ *B1 + 300 ppm Cl;* △ *B1 + 1000 ppm Cl;* □ *B1 + 1500 ppm Cl.*

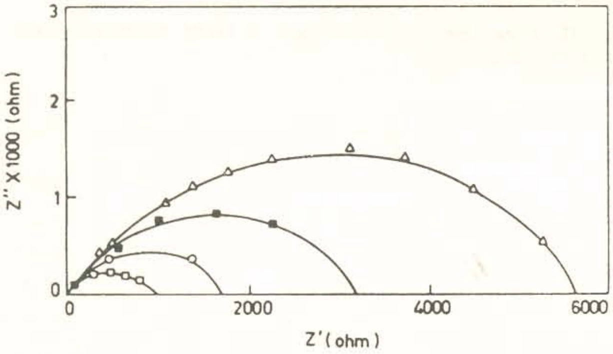

Fig. 9: Nyquist plot for brass in 0.1M NaOH after given immersion time. □ *15 min;* ● *60 min;* ■ *120 min;* △ *180 min.*

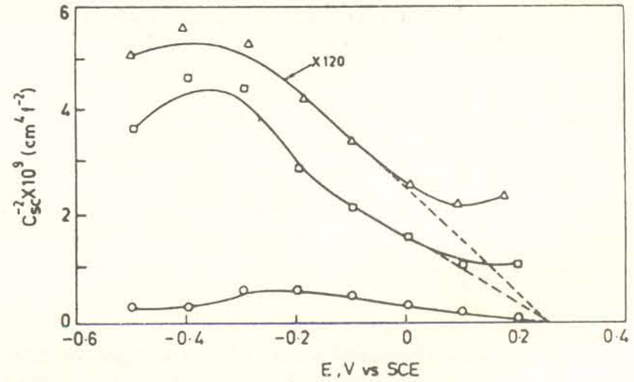

Fig. 10: Mott-Schottky plot for brass in 0.1M NaOH. ○ *10 Hz;* □ *100 Hz;* △ *1000 Hz.*

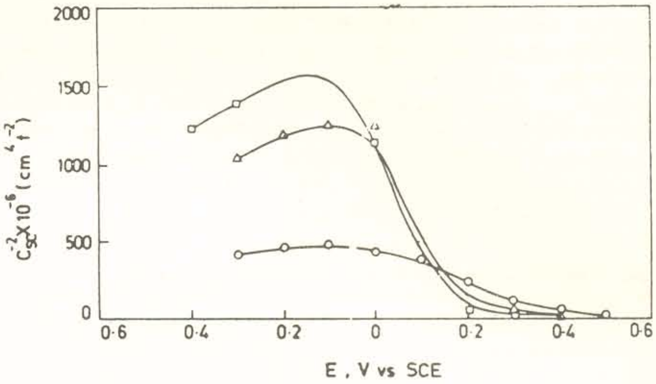

Fig. 11: Mott-Schottky plot for brass in 0.1M NaOH with addition of chloride. ○ *300 ppm Cl;* △ *1000 ppm Cl;* □ *1500 ppm Cl.*

TABLE-IV: Effect of chloride ions on V_{fb} and E_{bg} for brass in 0.1M NaOH

Medium	V_{fb} V	E_{bg} (eV)
0.1M NaOH	0.250	2.28
0.1M NaOH + 300 ppm Cl	0.350	2.65
0.1M NaOH + 1000 ppm Cl	0.180	2.62
0.1M NaOH + 1500 ppm Cl	0.160	2.70

Further addition of chloride ions decrease the photopotential. This is due to the domination of chloride ions in the film formation process, which may retard the action of OH^- ions. At the addition of 1000 ppm chloride, a critical concentration, the observed photopotential is less than that of the blank. When the concentration of the chloride ions is further increased, the photopotential also increases which may be due to the presence of CuO and cuprous chloride which are highly sensitive to irradiation.

(ii) Flat band potential measurements: The potential range of passivity of brass was found to be −0.5 V to +0.5V (SCE) and hence the capacitance was measured in this range. The extrapolation of the frequency dispersive Mott-Schottky plot (Fig. 10) intercepts the potential axis at 0.250 V, indicating the existence of an additional capacitance element in the interface. This may be arising from various types of inhomogenous charge accumulation including deep traps, surface states or non-stoichiometry of the oxide.

Table IV shows the effect of addition of chloride ions on flat band potential as calculated from Fig. 11. It has already been shown [25] that the addition of inhibitors shifts flat band potential considerably. It appears from the present study that chloride adsorption at low Cl^- activity inhibits the metal dissolution as suggested by Sato [26]. As the concentration of chloride is increased, the shift in flat band potential decreases and is much lower than in pure NaOH. This observation can be compared with photopotential measurements where the magnitude of photopotential is dependent on chloride concentration.

In both these cases, viz. pure NaOH and NaOH containing chlorides, bending of C_{sc}^{-2} curves at far negative potential ($V < V_{fb}$) indicates deep depletion or inversion nature and at more positive potentials ($V > V_{fb}$) the accumulation nature of the space charge layer.

(iii) Band gap measurements: The absorption spectra of the film formed on brass after immersion (1 h) in NaOH containing different chloride concentrations, given in Fig. 12 indicate that the addition of chloride decreases the absorption at all wavelengths and that new peaks are observed in presence of chloride. The decrease in adsorption is not uniform. This should be looked into in the light of other observations on photopotential and flat band potential.

The band gap measured for the various concentrations of chloride additions are given in Table IV.

CONCLUSION

The oxides formed on copper and brass in alkaline media behave like p-type semiconductors and the composition of the film varies with time in the case of copper. Formation of mixed oxides

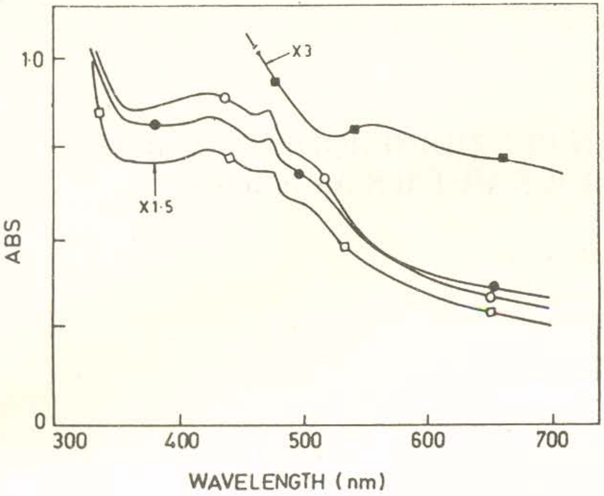

Fig. 12: Absorption spectrum for brass in 0.1M NaOH with addition of chloride. ■ Blank; ○ B1 + 300 ppm Cl; ● B1 + 1000 ppm Cl; □ B1 + 1500 ppm Cl.

on copper is hindered in the presence of inhibitors and the film is then essentially composed of a Cu_2O or a film of Cu_2O and a metal-inhibitor complex. Flat band potential and carrier concentrations are also reduced. Measurements carried out on rough surface clearly points out that the capacitance measurements must be restricted to one frequency only; otherwise the results will be complex in nature. The addition of chloride ions alters the photopotential and band gap significantly depending on the concentration in the case of brass.

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