

EFFECT OF CHLORIDE IONS ON THE SEMICONDUCTING PROPERTIES OF THE PASSIVE FILMS ON 304 STAINLESS STEEL

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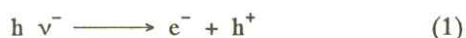
The electronic properties of the passive films play a major role in understanding of the metal/oxide/electrolyte interfaces. Presence of chloride ions either in atmosphere or in electrolyte are known for their aggressiveness and ability to cause pitting corrosion. The effect of addition of chloride ions on the semiconducting properties of the passive films formed on 304 SS are investigated by employing photoelectrochemical and capacitance measurements and the results are discussed.

Keywords: Passive film, 304 stainless steel and semiconducting materials

INTRODUCTION

The most sensitive surface techniques like ESCA, XPS, Auger, SIMS etc. have become valuable tools to study the structure and composition of the products formed on metal surfaces during passivation, but the application of these techniques suffers from their inability to analyse the films in situ. Knowledge about the electronic properties is quite important since it is a significant factor in determining the mechanisms of film formation and breakdown and the rate of metal dissolution. All the aforesaid processes involve movement of electrons and ions from the metal surface through the passive film or from the solution into the film. Also, the electron transfer reactions through the passive films depend strongly on the electronic properties of such films. Earlier investigations [1,2] reveal that the electronic properties of the passive films play a major role in controlling the corrosion resistance of the base metal.

Measurement of photocurrent, photopotential etc., by employing photoelectrochemical techniques give a complete picture about the semiconductive nature of the oxide films formed on metals and alloys. Capacitance measurements will also be useful in obtaining information regarding the electronic structure of the semiconductive passive films and by the analysis of the Mott-Schottky plots it is possible to obtain the flat band potential and the donor concentration [3]. 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 oxide/electrolyte interface is illuminated by a light having a photon energy $h\nu$ electrons can be excited from occupied to unoccupied states within the electrode, as:



The electron-hole formation according to the above expression is the basic reaction for photoelectrochemical

effects. These effects are often reflected as changes in the measured current or voltage.

Photoelectrochemical studies of the passive films on three different types of stainless steel reveal that the passive films are amorphous and highly disordered [4,5] and are of n-type in nature. Moreover it consists of oxyhydroxides of chromium and iron and its protective nature is dependent highly on the chromium content of the substrate alloy. Presence of chloride ions either in atmosphere or in electrolyte are known for their aggressiveness and ability to cause pitting corrosion.

In this paper an attempt has been made to study the effect of addition of chloride ions on the semiconducting properties of the passive films formed on 304 stainless steel by measuring the photopotential, flat band potential and the donor concentration.

EXPERIMENTAL

Two identical commercial grade austenitic stainless steel of 304 type which were polished, degreased and laquered to get a geometrical area of 1 cm^2 , were used as the electrodes for the photopotential measurement studies. The composition of these SS electrodes are as follows; Cr-19.15% (w/w), Ni-9.75%, C-0.08%, Mn-1.85%, Si-0.85%, P-0.045% and S-0.03%. The experimental procedures for the photopotential measurements are as described elsewhere [6]. These measurements were carried out in triple distilled water with the addition of chloride ions. Capacitance measurements were carried out using a conventional three electrode system with platinum as the counter electrode and saturated calomel as the reference electrode using PARC Electrochemical impedance system in sodium hydroxide medium with the addition of chloride ions. All the experiments were carried out in aerated conditions and at room temperature of $303 \pm 1 \text{ K}$. Solutions of AnalaR grade sodium chloride and sodium hydroxide in triple distilled water were used.

RESULTS AND DISCUSSION

a) Photopotential measurements

The potential difference (photopotential) between two identical SS electrodes were measured at a definite interval of time. Fig. 1 shows the photopotential measured with the addition of chloride ions to the distilled water at the end of 1st hour. According to Oshe and Rosenfeld [7], the photopotential of semiconductor electrode such as metal oxide can be represented as

$$V_{ph} = \frac{kT}{e} \ln \left(\frac{N_A}{N_D} \right) \quad (2)$$

where N_A , N_D are the concentrations of acceptor and donor defects and impurities respectively. For a metal oxide, the concentration of acceptor and donor correspond to those of excessive anion and cation to stoichiometric composition. This expression suggests that the n-type semiconductor electrode containing excessive cation (donor) shows negative sign photopotential, whereas the p-type semiconductor electrode containing excessive anion (acceptor) shows positive sign photopotential. The negative potential difference observed which is indicative of its n-type semiconducting nature, agrees with the Oshe and Rosenfeld model.

The magnitude of the observed photopotential is maximum at low chloride levels and it decreases with the increasing concentrations of chloride ions. This may be due to the adsorption of chloride ions on to the metal surface, leading to accumulation of negative charges at the oxide/electrolyte interface. As soon as the light is cut off, the observed photopotential difference falls much below the initial value. This may be due to the back reaction of the photogenerated species as suggested by Hardee and Bard [8].

b) Mott-Schottky plots

The capacitance of the passive film - electrolyte interface for 304 SS electrode in 0.1N NaOH and with the addition of chloride ions were measured as a function of frequency. For a semiconductor/electrolyte interface, the net capacitance C is related to the capacitance of the space charge layer C_{sc} and the capacitance of the Helmholtz layer C_H according to

$$\frac{1}{C} = \frac{1}{C_{sc}} + \frac{1}{C_H} \quad (3)$$

Normally, the capacitance associated with the Helmholtz region will be very large when compared to that of space charge region and therefore the total capacitance C will correspond to C_{sc} . The MS plots i.e. the $1/C^2$ vs potential plots were analysed using the expression for the space charge capacitance of a semiconductor in the depletion range

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left(V - V_{fb} - \frac{kT}{q} \right) \quad (4)$$

where ϵ is the dielectric constant of the film, N_D the donor concentration, V the applied electrode potential, V_{fb} the flat band potential and the remaining symbols have their usual meaning. According to the equation (4), the flat band potential of the passive film can be estimated by extrapolating the Mott-Schottky plots to the potential axis i.e. $1/C^2 = 0$ and the donor concentration can be calculated from the slope of the linear region. The calculation of donor concentration requires the knowledge of the dielectric constant of the films.

i) Influence of frequency

Fig. 2 shows the MS plot of 304 SS electrode in 0.1N NaOH at 10, 100, 1000 Hz respectively, exhibiting a strong frequency dispersion with different intercepts on the potential axis and with different slopes. Such types of behaviour was first observed by Dutoit *et al.* [10] for TiO_2 at $V \gg V_{fb}$. According to them, the linear region of the Mott-Schottky plots exhibits two types of behaviour. In the A-type behaviour, both the slopes and the potential intercepts vary with frequency, although the linear region of the MS lines are parallel. In B-type behaviour, the slopes vary but all the lines coverage to a single intercept on the potential axis.

From Fig. 2, it can be clearly seen that the shift in V_{fb} is in the negative direction with the increasing frequency and that the slope of the linear region is also different. Hence this type of behaviour may be classified under A-type. This may be attributed to the formation of thin disturbed layer confined to the surface where as B-type behaviour requires that the disturbed layer extent to the full width of the diffusion layer. Several authors [11-13] have explained these type of frequency dispersion by considering suitable R-C circuit models. Generally these models will consist of more complex circuit with additional elements in parallel to the space charge capacitance and many of them will be frequency dependent. The additional elements mentioned here are mainly for depicting the surface state impedances. According to Finklea [14], that any circuit model which contains more

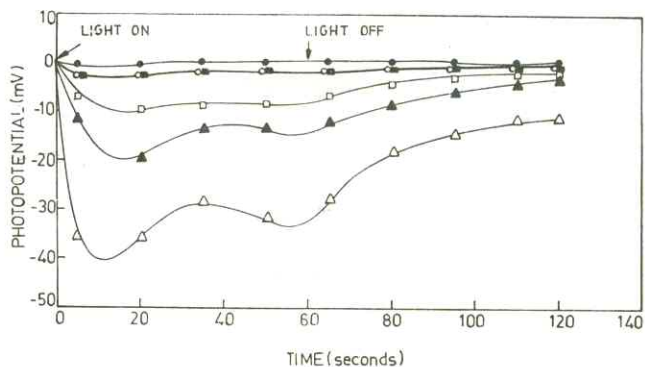


Fig. 1: Photopotential measured for 304 SS electrodes at the end of 1st hour in

- Distilled water
- ▲ + 100 ppm chloride
- + 700 ppm chloride
- △ + 50 ppm chloride
- + 500 ppm chloride
- + 1000 ppm chloride

than four elements viz., the space charge capacitance, the Helmholtz capacitance, the series resistance and the faradaic resistance, requires separate experimental evidences to justify the incorporation of the additional elements. Hence to avoid such instances, care should be taken in the experimental procedures and the electrode preparation.

The flat band potential and donor concentration obtained from the MS plots at 1 KHz are -830 mV and $1.5 \times 10^{21} / \text{cm}^3$, which agrees with that of Di Paola [4]. However, the value of N_D is high, due to the highly disordered and amorphous nature of the film.

ii) Effect of addition of chloride ions

Table I shows the measured V_{fb} and the donor concentrations of the passive film on 304 SS in 0.1N NaOH with chloride ion additions. For comparison of the results, the donor concentration and V_{fb} value were calculated from the capacitance measurements obtained at 1 KHz. The dielectric constant assumed for the calculation of N_D is 15.6 [4].

Addition of chloride ions at low levels shifts the V_{fb} appreciably in the cathodic direction when compared to that of 0.1N NaOH. Further addition of chloride shifts the V_{fb} in the anodic direction, similar to that of brass [6] wherein low level chloride addition inhibits the corrosion process. The donor concentration continues to decrease with the addition of chloride ions.

According to Chao [15], thin passive films may have many lattice defects and the amorphicity of the passive films decreases with increasing film thickness. These results indicate that the film formed at 0.1N NaOH is thin and highly amorphous. The thickness of the film is considerably increased at low chloride levels as observed from the higher N_D values. This may be the reason for the shift in V_{fb} at low chloride levels. Further addition of chloride decreases the donor concentration, indicative of the increase in the amorphicity and decrease in the thickness of the film. These results are in good agreement with the observed photopotential measurements i.e. the larger magnitude of the photopotential at low levels of chloride addition is due to the thickening of the film. Beyond 3000 ppm of chloride addition, presence of depletion layer could not be observed.

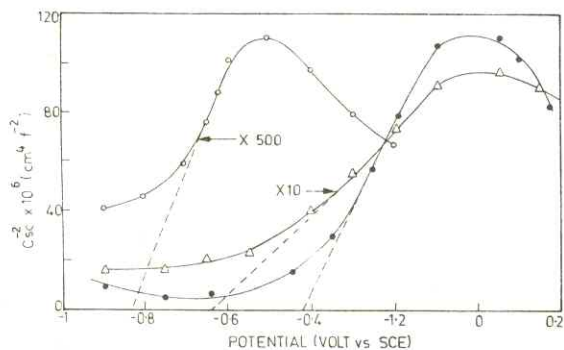


Fig. 2: Mott-schottky plot for 304 SS in 0.1 N NaOH
 ● 10 Hz ▲ 100 Hz ○ 1000 Hz

TABLE I: Effect of chloride ions on flat band potential and donar concentration (at 1 kHz)

Medium	V_{fb} (mV)	N_D ($\times 10^{21} \text{ cm}^{-3}$)
0.1 N NaOH	-830	1.523
0.1 N NaOH + 50 ppm Cl^-	-1261	6.347
0.1 N NaOH + 100 ppm Cl^-	-1253	5.985
0.1 N NaOH + 300 ppm Cl^-	-1137	4.147
0.1 N NaOH + 500 ppm Cl^-	-1067	3.719
0.1 N NaOH + 700 ppm Cl^-	-1069	1.410
0.1 N NaOH + 1000 ppm Cl^-	-1062	1.648
0.1 N NaOH + 3000 ppm Cl^-	-966	0.436

CONCLUSION

Though the film formed on 304 SS exhibits the properties of n-type semiconductor, its electronic properties vary considerably with the surrounding electrolyte. The main reasons for the frequency dispersive nature of the films may be due (i) to amorphous nature of the passive film, (ii) to a non-uniform distribution of donors and (iii) to the formation of thin disturbed layer confined to the surface ("A" type behaviour in the MS plot). The thickness of the passive film increases at low chloride additions due to the dehydration of the oxides at surface leading to the accumulation of excess hydroxyl ions at the oxide/electrolyte interface. Further investigations are in progress to understand the role of other halide ions like Bromide, Iodide etc., on the semiconducting properties of the passive films on 304 SS.

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