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INSITU STUDY OF METAL SURFACE BY OPTICAL LIGHT REFLECTION

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ABSTRACT

Passive oxide films formed on metal surfaces can be broken by the addition of aggressive ions like chloride while these films reinforced or prevented from being broken down by the addition of inhibitors. This can be examined by monitoring the changes in the reflectivity of the surface. The nature of the passive films formed has been studied by optical reflection in NaCl-NaOH and NaCl-sodium benzoate media for a mild steel electrode.

Likewise metal ions are used to reinforce corrosion inhibition or as inhibitors. Such cations are thought of as being deposited as monolayers at potentials more positive than the reversible Nernst potentials. The monolayer formation of lead on a mild steel surface from solutions containing Pb^{++} has also been examined by monitoring the reflectance changes.

INTRODUCTION

Electrochemical reactions, corrosion not to be excluded, occur at the metal/solution interface. For examining the interface *in situ* during various electrochemical reactions such as corrosion, classical optical reflection methods have been found to be of great use. Light penetrates up to about 50 atomic distances ($\sim$ 10 nm) into a metal making it suitable for examining the entire depth of the film. Although individual details of molecular processes on the surface cannot be solved on a scale much smaller than the wavelength of the incident radiation, optical techniques can nevertheless be employed to monitor changes in surface coverage at the sub-mono layer as a result of the extreme sensitivity of the reflection coefficients to small changes in phase angle. In addition, the wavelength selectivity and rapid response of these methods facilitate kinetic and mechanistic studies of surface processes. Further the optical techniques are non-destructive and greatly facilitate not only better understanding of the events at the interface by providing supplementary information but also form one of the few essential tools for understanding all aspects. For instance, it is difficult to know by the observation of current alone whether anodic dissolution of the film or that of the substrate metal takes place, but this can be readily known from reflectance measurements. Likewise, detection of pitting under normal conditions can be done more easily by reflectance method than by electrochemical methods. Considerable additional information has also been obtained on adsorption of anions or organic compounds, passivation of metals, formation of metal monolayers etc.; so much so, these techniques have become a common tool in the hands of researchers.

PRINCIPLE INVOLVED

In the optical reflection method, a quantitative comparison is made between the properties of incident and reflected light on a well polished electrode surface and the changes in amplitude (E) and phase (Δ) are followed. The reflection methods can be broadly divided into three categories:

i) Internal reflection method,
ii) Specular reflection method, and
iii) Ellipsometry

In the reflectivity measurements, the reflectivity $R_{\parallel}$ and $R_{\perp}$ are obtained using light polarised in the parallel and perpendicular directions respectively.

For examining the interface *in situ*, specular reflectance [1] with a monochromatic beam in the energy range of 0-25 eV can be used. In this technique, the ratio of the intensity of reflected beam to that of the incident beam at the interface between metal surface and electrolyte is dependent on surface conditions at the interface. Both polarized and unpolarized beams can be used. For monitoring the changes in reflectance, the quantity of percent change in reflection (PCR) ie. $\frac{\Delta R}{R_o}\%$ is measured. Here R_o is reflectance at the start of an experiment when no film is present on the surface, and R is reflectance at any subsequent stage, $\Delta R = (R_o - R)$ is a change in reflectance and R_o and R are identified with intensity of reflected light. PCR can be as low as 10^{-5} in the case of polarised light. Here, changes in PCR can be related to surface reflectivity. An increase in PCR indicates a decrease in surface reflectivity. The increase in PCR usually indicates film growth and a decrease in PCR indicates film dissolution. Further the nature of the film can be examined by recording changes in PCR at various photon energy ranges. The presence or absence of certain constituents in the film can be confirmed from the photon wavelength variation of PCR if these constituents have characteristic reflection maxima or minima at various wavelengths. Thus, by applying specular reflectance technique, information about films formed at metal-electrolyte interface can be obtained.

When a metallic electrode is immersed in a corrosive-passive medium containing chloride ions and inhibitor molecules, film formation on the metallic surface occurs. Passive films on the surface can be broken down by the chloride ions when the concentration exceeds a critical value. Such film formation produces changes in the reflectance of the surface. Thus, by monitoring the surface reflectance, information about the surface films can obtained [1]. Likewise, the films formed by electrochemical deposition at appropriate potential from solutions containing metal cations such as Pb^{++}, Cd^{++} etc., can also be studied by monitoring changes in surface reflectance [2].

In this paper, the study of film formation on mild steel surface under two different sets of conditions is reported.

i) Mild steel surface immersed in chloride-inhibitor media where variation of surface reflectance both with time and with potential has been studied.

ii) Mild steel surface immersed in solutions containing milli-molar concentrations of Pb^{++} ions where surface reflectance changes produced by deposition and dissolution of metal monolayers have been examined.

EXPERIMENTAL

The chloride-inhibitor media were prepared by dissolving various concentrations of sodium chloride and sodium hydroxide or various concentrations of sodium chloride and sodium benzoate. The concentrations ranged from 0 - 320 ppm for chloride, 0 - 1000 ppm for NaOH and 0 - 2000 ppm for sodium benzoate. Unpolarized visible wavelengths centred at 425, 550 and 670 nm obtained by filtering the output from a high pressure mercury vapour lamp were used as light sources for observing reflectance changes.

For monolayer formation studies, solutions containing 10^{-2} to 10^{-4} M of Pb^{++}, Cd^{++} were used. The solutions were prepared from Analar (BDH) grade chemicals using double distilled water.

Light detection was through a light-dependent resistor which was part of the circuit producing a voltage proportional to the light reflected from the surface. A configuration in which the experimental electrode surface (immersed in the experimental medium) was oriented at 45° to both the source light beam and the reflected beam was employed. Before the start of each experiment, the electrode surface was polished to produce a mirror-finish. For potential scan studies, the potential was scanned in the range −1.00 to +0.4V with respect to SCE at 1 mV/sec. using a Wenking potentioscan unit.

RESULTS AND DISCUSSION

i) Reflectance-time studies : Figures 1 and 2 show the variation of PCR with time in NaCl-NaOH and NaCl-Na benzoate media.

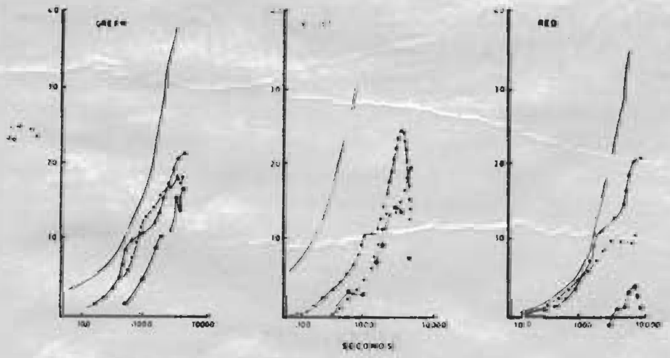

Fig. 1 : Variation of percent relative reflectance change with time in different spectral regions for mild steel in NaCl - NaOH media

In ppm : — 100 NaCl; —x—x—x 100 NaCl + 20 NaOH
—·—·— 10 NaCl + 40 NaOh; —o—o—o 100 NaCl + 60 NaOh

PCR is found to vary logarithmically with time in solutions containing only Cl^- ions, in agreement with the report [3] which showed that the growth of an oxide film on iron follows a logarithmic law.

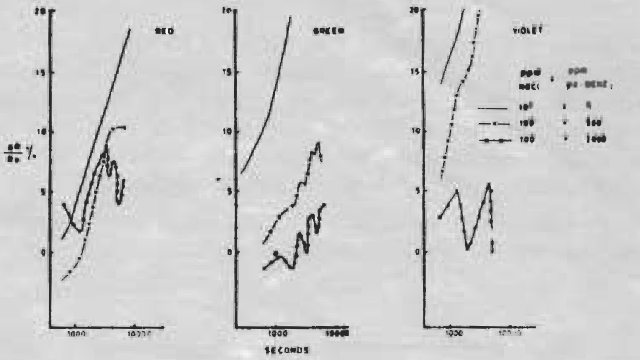

Fig. 2 : Variation of relative reflectance change with time i different spectral regions for mild steel in NaCl - Sodiu Benzoate media.

When the concentration of the inhibitor increases, the film growt rate deviates from the logarithmic law because of adsorption o the inhibitor or formation of a film on the surface as in the case o sodium benzoate [4].

Larger changes in PCR occur at the end of equal time intervals a 425 nm than at 550 nm or at 670 nm. Initially PCR at 550 nm i slightly greater than at 670 nm. It is known that Fe^{++} reflect well in the green while Fe^{+++} reflects predominantly in the re [5]. The results (Figures 1 and 2) indicate that initially Fe^{++} an Fe^{+++} exist in equal amounts (similar PCR values at 550 an 670 nm) while after 1000 secs. there is predominance of Fe^{++} ions. This is inferred from lower values of PCR (ie. highe reflection) at 670 nm as compared with 550 nm at the end o 1000 secs.

ii) Reflectance-potentioscan studies: Figure 3 shows the reflec tance changes in NaOh-NaCl system under potentiodynami

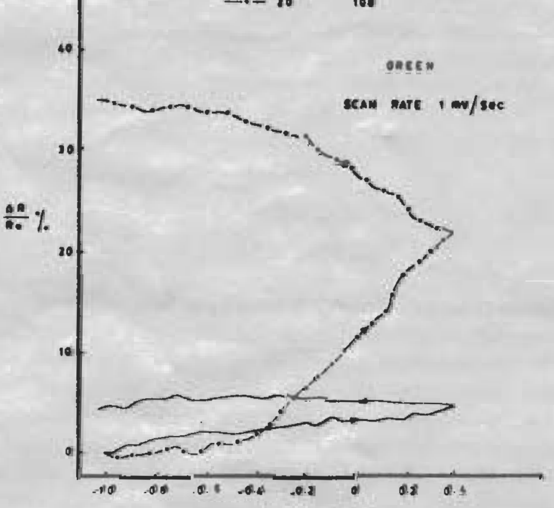

Fig. 3 : Variation of percent relative reflectance change with potential for mild steel electrode in NaCl - NaOH medi in the green region.

conditions at 550 nm. When OH^-/Cl^- is 25 there is not much change in PCR, suggesting complete passivity of the system. When this ratio is only 5, passivity occurs only over a narrow range and complete dissolution starts at −0.4V since reflectivity continuously decreases for this wavelength. Iron essentially goes into solution as Fe^{+++} ions under these conditions.

Figure 4 shows the reflectance changes under potentiodynamic conditions for the NaCl-sodium benzoate system. It is seen that PCR changes much less for green (550 nm) than for violet (425 nm) indicating the mediation of Fe^{++} ions in the dissolution process in this case.

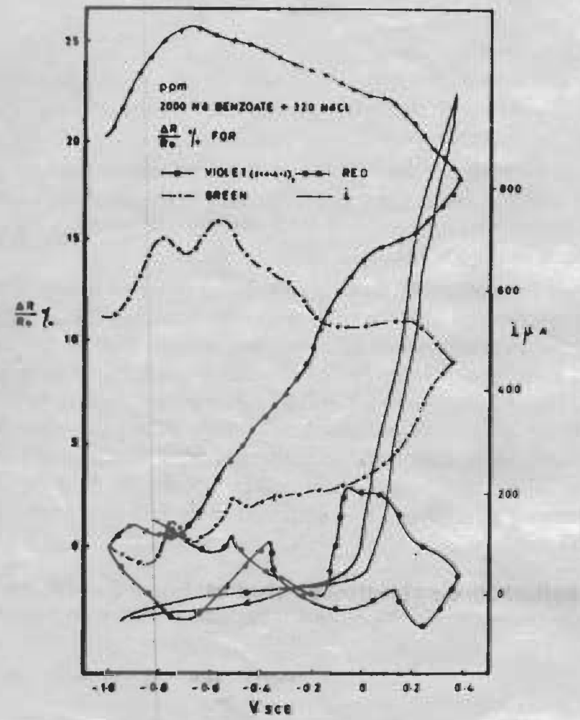

Fig. 4 : *Variation of current and percent relative reflectance change with electrode potential V sce for mild steel in NaCl - sodium benzoate media in different spectral regions.*

Reflectance changes during monolayer formation: Figure 5 shows the reflectance changes as the potentials of the mild steel electrode was scanned from −0.3V to −0.9V. It is observed that there is a sudden change in the slope of reflectivity at −0.5V, indicating the deposition of monolayer thickness of metal. The changeover from monolayer to bulk deposition is indicated by a similar change in slope of PCR curve at −750 mV. These results were obtained for a scan rate of 10 mV/sec. For a slower scan rate of 1 mV/sec. the potentials for monolayer and bulk depositions rise to more positive values. This dependence on the scan rate indicates that the reversibility of the process is assured only at slow scan rates. The changes in PCR are also different for the three wavelength used.

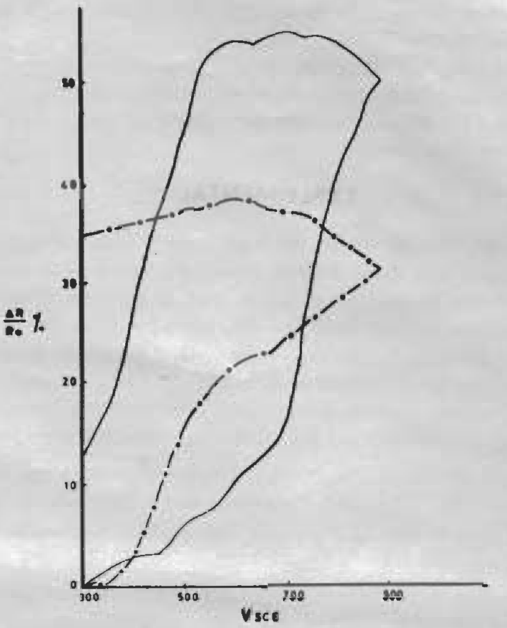

Fig. 5 : *Variation of percent relative change in reflectance with electrode potential in the violet region.*

— 1mV/sec, —·— 10mV/sec

CONCLUSION

It has been shown that film formation processes at a given surface immersed in various experimental media can be monitored *in situ* by observing changes in reflection.

It has been observed that Fe^{++} ions take part in the dissolution process in presence of benzoate for the mild steel electrode while only Fe^{+++} ions play a role when only OH^- ions are present.

The study of deposition and stripping of lead monolayer examined by this method indicates that this process is not wholly reversible at high scan rates.

Thus the growth of non-metallic and metallic films on metal surfaces can be studied by reflection.

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