Electrochemical & optical characterisation of passive films on stainless steels

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Abstract. The formation and breakdown of the passive film are mainly controlled by ionic and electronic transport processes; processes that are in turn controlled by the electronic properties of the film. Consequently a comprehensive understanding of mechanisms behind passivity and localised corrosion require a detailed perception of the electronic properties of the passive films together with compositional and structural information. As a step towards this goal the passive film on austenitic stainless steel, AISI 316L, formed in borate solution was characterised by in situ Raman spectroscopy and photocurrent spectroscopy coupled with electrochemical measurements. The composition, structure and semiconductivity of the passive films depended on the potential; Fe rich n-type oxide and a Cr rich p-type oxide dominated at more positive potentials and more negative potentials respectively whilst n-type dual layered film formed at intermediate potentials. Analyses of the bandgap determined for these oxides suggested their structures to be Fe$_2$O$_3$ and a Fe-Cr spinel. This hypothesis was supported by the results of in situ Raman spectroscopy.

1. Introduction

The corrosion resistance of stainless steel arises from a "passive" chromium-rich oxide film that forms on the surface. Although extremely thin, less than 5nm, this protective film is strongly adherent and chemically stable. Nevertheless in certain environments, especially ones containing chloride, this oxide film will breakdown and rapid corrosion will ensue.

One of the principal factors to thought to control the behaviour of a passive film is its electronic properties. The formation and breakdown of the passive film layer are mainly controlled by ionic transport reactions and electronic transport reactions. Both of these are controlled by the energetics of the metal/film and film/electrolyte interfaces and the electronic properties of the passive film. Consequently it is indispensable to comprehend the electronic properties of the film before the mechanism behind localised corrosion processes can be fully understood.

The invention of several optical spectroscopical techniques has intensified the potential of examining the characteristics of the film to a better extend of accuracy. In particular Di Quarto et al. have developed empirical relationships, based on anion and cation electronegativities, which allow the composition of simple oxides and hydroxides to be related to experimentally determined bandgaps.[1] The approach in this paper is to use in situ photocurrent spectroscopy to determine the bandgaps of the

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oxides in the passive film on 316L stainless steels, use the theory of Di Quarto et al. to propose compositions and then support these claims with in situ Raman spectroscopy. Thus an in depth understanding of the electronic properties of the passive film together with its structure and composition will be revealed.

2. Experimental
The specimens were fabricated from the 316L stainless steel; the nominal composition of which is shown in Table 1. The specimens were ground consecutively with 600 grit and 1200 grit SiC paper and were further polished with alumina polishing powder down to 0.1 micron. Samples were then cleaned in deionised water and degreased in ethanol. The electrolyte was 0.1M Na₂B₄O₇.10H₂O (pH 9.2); prepared in de-ionized water using reagent grade chemicals. Before any experiment was carried out, the electrolyte was deoxygenated with high purity nitrogen gas for one hour. A saturated calomel reference electrode was used and all potentials quoted in this paper are versus this system. The counter electrode was a platinum grid.

| Table 1. Nominal chemical composition of 316L stainless steel. |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Cr | Ni | Mo | Mn | Si | C | P | S |
| 16.0 - 18.0 | 10.0 - 14.0 | 2.0 - 3.0 | 1.0 - 2.0 | 0.5 - 1.0 | 0.04 - Max | 0.006 - 0.03 |
| 1.0 | 2.0 | 1.0 | 0.5 | 1.0 | 0.04 | 0.006 |

Photoelectrochemical measurements were performed by using a 300W xenon lamp and a monochromator. The photocurrents were generated by focusing the light with a fused silica lens thorough a quartz window of the electrochemical cell onto the working electrode. The lock-in amplifier technique was used to separate the photocurrent from the passive current by chopping the light at 29Hz. The measuring procedure was that first the film was grown potentiodynamically at a rate of 10mV/min from -900mV(SCE) up to 800mV(SCE). Then photocurrent spectra were obtained as the potential was brought back in the negative direction, the potential being held constant during the course of each measurement. The wavelength of the light was changed in steps of 10nm. The photocurrent was corrected for the output of the lamp and the efficiency of the monochromator by using a calibrated photodiode. Calibration was performed before and after every set of experiments.

For in situ Raman spectroscopy a specially designed electrochemical glass cell produced by Ventacon with a quartz window to accommodate a three electrode system was used. The surface enhance Raman spectroscopy (SERS) technique was used to overcome the weak intensities of peaks which restrict the detectability.[2] The silver deposition required for SERS was performed, after polishing and cleaning immediately prior to the Raman experimentation. A Dilor–Jobin HR 800 confocal Raman spectrometer with argon ion green laser (514.5 nm) operating at 40mW was used. The spectral resolution of the Raman instrument was ±2.5cm⁻¹. Raman spectra were recorded at each 100mV interval and the observed peaks were compared with literature values [3-10] for identification of phases present.

3. Results and discussion
3.1. Bandgap estimations
The simplified relationship between photocurrent (Iₚₚ) and the bandgap (E₉) of the amorphous passive films can be written in the form;

\[(Iₚₚhv)^{1/n} = const.(hv − E₉)\]  

where \(hv\) is the energy of the photon, \(A\) is a constant and the value of \(n\) depends on the nature of the optical transition; where \(n=2\) for the non-direct transition of amorphous semiconductors.[11] Subsequently the bandgap values obtained from Equation (1) were analysed according to the theoretical model developed by Di Quarto et al. to determine the nature of the oxides present.[1] To
aide interpretation the photocurrent spectra recorded from 316L stainless steel have been categorised into three main voltage regions.

3.1.1. Region (a). From 800mV to 400mV: showed a positive photocurrent (hence an n-type semiconductivity), a single bandgap near 1.95±0.5eV. These experimental bandgap estimations are in agreement with the bandgap values previously found for Fe₂O₃ and Fe(OH)₃. [1]

3.1.2 Region (b). From 200mV to -300mV: showed positive photocurrent (n-type) and analyse according to equation (1) indicated the presence of two different bandgap values; one at 1.95±0.05eV and the second at 2.9±0.05eV (Figure 1). A comparison of the theoretical and literature values for the bandgaps of possible oxides yield a best fit with an Fe-Cr spinel, FeCr₂O₄, which has a theoretical band gap of 3.0eV. [1] On scrutinising the equations and relationships the Di Quarto et al. model this small discrepancy between the theoretical and experimental bandgaps could be interpreted as due to the existence of Fe(III) in the spinel structure; which make decrease the bandgap. Therefore the spinel structure perhaps should be represented in a more accurate formula as Fe(II)[Cr(III)xFe(III)(1-x)]₂O₄ with the value x being estimated as 0.85.

3.1.3. Region (c). From -450mV to -900mV: no photocurrent could be observed between -450mV and -600mV, indicating the possible location of the flat band potential. Below -600mV the photocurrent switched signed to become negative, signifying p-type semiconductivity. A single bandgap value obtained in this potential region was 2.9±0.05eV; identical to that found for the wide bandgap n-type material formed in the region (b). The types of semiconductivity (p or n) were also confirmed with photocurrent transients and Mott-Schottky plots.

![Figure 1](image-url)

Figure 1. \((I_{ph}h\nu)^{0.5}\) vs. \(h\nu\) plot for 316L in borate solution at -100mV(SCE). Two linear extrapolations give two different bandgap values, 1.9eV and 2.9eV respectively.

3.2 In situ Raman results

Table 2 shows the phases identified in in situ Raman for the same potential ranges used for the photocurrent spectroscopy. Excellent agreement between the two techniques was obtained. The only Raman also identified a Cr(VI) oxide in the transpassive region, which was not detected by the photocurrent measurements, indicating that it is not a semiconductor and thus it is probably an insulator.

Based on all the data obtained from Raman spectroscopy, photocurrent measurements and the cyclic voltammograms it is believed that the most likely oxide phases on the 316L stainless steel at different potentials are as shown in Table 3.
Table 2. The summary of the Raman spectroscopy results obtained for 316L in borate solution. Oxygen / hydrogen gas evolution prevented collection of Raman spectra beyond the range -900mV to +800mV.

| Potential range | Raman shift | Possible oxide phase | Remarks          |
|-----------------|-------------|----------------------|-----------------|
| 800mV to 400mV  | 838 cm$^{-1}$, 890 cm$^{-1}$, 933 cm$^{-1}$, 228 cm$^{-1}$ to 230 cm$^{-1}$ | Cr(VI) oxide     | Possibly Fe$_2$[CrO$_4$]$_3$ |
| 200mV to -300mV | 690 cm$^{-1}$ to 700 cm$^{-1}$, 228 cm$^{-1}$ to 230 cm$^{-1}$ | Fe-Cr spinel     | Possibly FeCr$_2$O$_4$ |
| 100mV to -900mV | 690 cm$^{-1}$ to 700 cm$^{-1}$ | Fe-Cr spinel       | Likely Fe$_2$O$_3$, as not seen below -500mV. |

Table 3. Summary of the phases that are believed to form, their bandgap values and semiconductivities at different potential of 316L in 0.1M borate solution.

| Potential range | n/p type | Bandgap (eV) | Suggested oxide                              |
|-----------------|----------|--------------|----------------------------------------------|
| -800mV to -900mV| p-type   | 2.9±0.05     | Fe(II)[Cr(III)$_{x}$Fe(III)$_{(1-x)}$]O$_4$; 0<x<1 |
| 200mV to -300mV | n-type   | 1.95±0.05    | Fe(III)oxide (probably Fe$_2$O$_3$)             |
|                 | n-type   | 2.9±0.05     | Fe(II)[Cr(III)$_{x}$Fe(III)$_{(1-x)}$]O$_4$; 0<x<1 |
| 400mV to 800mV  | n-type   | 1.95±0.05    | Fe(III)oxide (probably Fe$_2$O$_3$)             |
|                 | insulator| -            | Fe$_2$[CrO$_4$]$_3$                             |

4. Conclusion

Photocurrent spectroscopy and in situ Raman spectroscopy have been used to reveal the nature and the potential dependence of the structure and the composition of the passive film formed on 316L stainless steel. It was found that in the passive region the film consists of two n-type oxides, most likely Fe$_2$O$_3$ and a Fe-Cr spinel thought to be Fe(II)[Cr(III)$_{0.85}$Fe(III)$_{0.15}$]O$_4$. At extreme negative potentials the Fe-Cr spinel is able to switch to p-type behaviour. In the transpassive region the spinel is oxidised to a Cr(VI) compound, whilst the Fe$_2$O$_3$ remains intact.

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