

## X-ray photoelectron spectroscopy for surface film analysis in corrosion research

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**Abstract.** Surface films on metals and alloys often protect them from reaction with the environment, and hence a knowledge of their protective properties and composition could be invaluable for predicting their corrosion behaviour. XPS (x-ray photoelectron spectroscopy) could provide a quantitative analysis of the chemical composition, the nature of valence states and elemental distribution within the surface films.

The present paper reviews the potential of this technique in corrosion studies. A brief review of the work done on the passivation of iron and iron-chromium alloys and on the inhibition studies on copper base alloys has been given. A few examples of investigations carried out at authors' laboratory are also included. An attempt has been made to establish a correlation between the compositions of the films formed and corrosion behaviour of carbon steel in 10.5 pH lithium hydroxide solution and of Cu-Ni alloys and sacrificial Al-Zn-Sn alloys in synthetic sea-water.

**Keywords.** X-ray photoelectron spectroscopy; surface film; passivation; inhibition; pitting; sacrificial anodes.

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### 1. Introduction

Most of the engineering metals and alloys possess a high degree of corrosion resistance due to the presence of surface films which are often adherent, tenacious and resistant to attack by the environment. The surface properties are very important as every type of reaction, be it solid-solid, solid-liquid or solid gas, commences at the surface. For example austenitic stainless steels are resistant to attack due to the presence of a chromium rich passive layer. Ni-Cr alloys (15 to 20% Cr) possess high temperature oxidation resistance due to the formation of a protective  $\text{Cr}_2\text{O}_3$  or  $\text{NiCr}_2\text{O}_4$  scale. Further, corrosion inhibition studies have indicated that inhibitors often change the surface film to provide better protection. A mention may be made of the formation of copper-benzotriazole complex on copper and copper-nickel alloys in the presence of benzotriazole inhibitor in an aqueous medium.

The study of the surface composition and property correlations provides basic guidelines to understand the various types of corrosion failures like localised attack, intergranular corrosion, stress corrosion cracking etc. Though other conventional methods of corrosion evaluation like weight change, electrochemical measurements etc have been in use, x-ray photoelectron spectroscopy (xps) has emerged as one of the most powerful tool for the study of composition of 2-3 nm thick corrosion films. The technique was first developed by Siegbahn (1967) who had earlier shown the possibility of distinguishing from the photoelectron spectrum, an element in different valence state. Since then, xps has been utilised in a variety of research problems in a number of laboratories. In xps, all the energy of the incident photon is expended in the ejection of

the photoelectron. Thus, the binding energy ( $E_B$ ) of the electron with respect to Fermi level can be determined by the relationship:

$$h\nu = E_{\text{photo}} + E_B + Q, \quad (1)$$

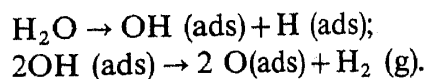
where  $E_{\text{photo}}$  is the kinetic energy of the photoelectron and  $Q$  is the work function of the spectrometer material. The energy of the photon,  $h\nu$ , is a known quantity.  $E_B$  assumes different values for different electronic shells and it is to some extent, dependent on the chemical state of the atom. Consequently, the energies of the ejected photo-electrons may be shifted slightly as the chemical state is changed. Shifts in core binding energies can be measured and related to the chemical environment. Studies of the satellite structure in the spectra, measurement of relative intensities as well as energies of photoelectron peaks and determination of the angular distribution of the expelled photo-electrons could provide useful information about the chemical species. xps has thus attracted the attention of the corrosion scientists, as the technique is capable of analysing few monolayer thick films, which cannot be analysed by other techniques. Thus, the action of inhibitors and the phenomenon of passivation can now be understood in a much better way.

As already mentioned xps spectrum of an oxide can be distinguished from that of the parent metal. In many cases, it is possible by observing the chemical shifts (Castle and Epler 1974; Hoare and Talerman 1972; McIntyre and Zetaruk 1977; Asami and Hashimoto 1977; Allen *et al* 1974), peak shapes (McIntyre and Zetaruk 1977), multiplet splitting (Carver 1972) and presence or absence of satellites (Castle 1971). Hydroxides (McIntyre *et al* 1976) and chlorides (Belton and Clarke 1976; Kishi and Ikeda 1974) can also be identified. Carbon in carbidic form can also be distinguished from that due to hydrocarbon contamination (Ramqvist 1970). One difficulty that frequently arises in xps characterization of corrosion products is that the oxide film formed in aqueous solution on certain metals and alloys may be susceptible to further atmospheric oxidation (before introducing the specimen into the vacuum chamber of the spectrometer) and one may end up with erroneous conclusions. In addition, valence state determination of the oxide is meaningless after  $\text{Ar}^+$  ion bombardment unless the oxide has been checked for stability.

## 2. Brief review of corrosion research using xps

### 2.1 Passivation studies on iron and its alloys

Several studies have been reported on the passivation of iron and iron-chromium alloys. Roberts and Wood (1977) have investigated the mechanism of oxidation and passivation of iron by water vapour using xps. The authors have studied the interaction of water vapour with iron at 290 K by xps and have found clear evidence for the passivation of surface. The O 1s peak observed at 530 eV has been assigned to the oxygen chemisorption or a surface oxide while that at 532 eV to the OH (adsorbed) species. The peak at 534 eV has been related with the molecularly adsorbed water. After having established the presence of both  $\text{OH}^{\delta-}$  and  $\text{O}^{\delta-}$  species, the authors have suggested that the first step is the dissociation of water followed by interaction between the surface hydroxyls to give chemisorbed oxygen:



A significant feature of the study was that the ratio of the intensities of the 530 and 532 eV peaks remained similar upto the maximum water exposures. It was therefore suggested that a discrete chemical phase of FeOOH existed on the surface as a result of passivation.

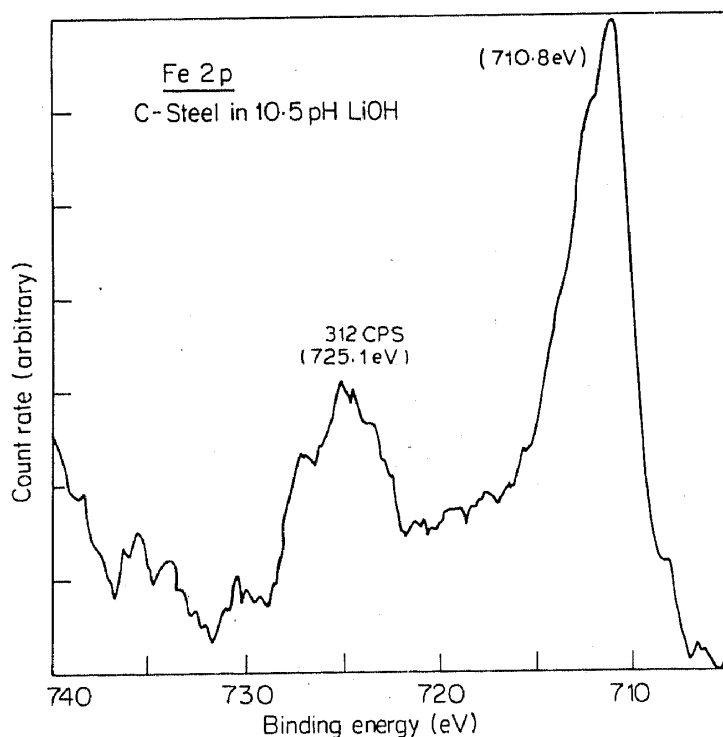
XPS studies on the electrochemical passivation of chromium (Bouyssoux and Romand 1977) in 0.5 M  $\text{H}_2\text{SO}_4$  at +0.55 V/NHE for 90 minutes indicated two spin doublets Cr  $2p_{1/2}$  and Cr  $2p_{3/2}$ . The higher binding energy of  $2p_{3/2}$  peak (575.6 eV) has been assigned to the oxide while lower binding energy (573.1 eV) to the metal. These peaks have been compared with those of standard oxides of chromium and it has been concluded on the basis of O 1s peak at 529.4 eV that the formation of anhydrous phase of  $\text{Cr}_2\text{O}_3$  takes place as a result of passivation.

Asami *et al* (1978) have reported the composition of passive film formed on an extremely corrosion-resistant amorphous alloy of iron (Fe-10 at. % Cr-13 at. % P-7 at. % C), in 1 N HCl as a result of passivation by immersing for 168 hours at 30°C. The study indicated that the air-formed film on the alloy mainly consisted of ferric oxyhydroxide. However, on immersing in HCl, chromium peak at 577 eV dominated and the traces of iron in the film existed both in  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states. The chromium peak at 577 eV has been attributed to oxidised chromium. The low binding energy peak of O 1s spectrum (metal-O bond) shifted after immersion from 530.2 eV to 530.6 eV. The peak at 530.2 eV has been assigned to Fe-O bonds in the air-formed film while that at 530.6 eV to Cr-O bonds in the passive film. Relatively high intensity in the high energy peak of O 1s spectrum of the air-formed film, which has been assigned to large amount of OH groups, decreased in intensity by immersing into HCl. The authors have assigned this observation to the formation of a homogeneous, hydrated chromium hydroxide  $\text{CrO}_x(\text{OH})_y \cdot n\text{H}_2\text{O}$  and thus causing passivation of the surface. Asami *et al* (1978) have further investigated the passivity of a series of iron-chromium alloys in sulphuric acid reported that chromium content of the passive film increased drastically at ca 13 at. % Cr of the bulk alloy composition whereas no composition change occurred in the surface of the substrate alloy immediately under the passive film. The high corrosion resistance of iron-chromium alloys with high chromium content has been attributed to the protective nature of hydrated chromium oxyhydroxide which is the main constituent of passive films in alloys containing chromium at least 12.5 at. %.

Chance and Gaarenstroom (1980) have characterised the surface films formed on a ferritic stainless steel (SAE type J 409) in sodium sulphate solutions of differing pH as a function of polarization potential. The study showed that the critical current for passivation was extremely sensitive to pH, *e.g.* with 0.5 M sulphate solutions at 82°C, the critical current for passivation increased by more than two orders of magnitude as the pH changed from 3.0 to 2.8. XPS investigations indicated that composition and thickness of a surface film changes significantly during anodic polarization but the most noteworthy was the change from the films of iron and oxygen in the prepassive region into the chromium and oxygen films in the passive region. The films which were initially made of Cr and O did not change above primary passivating potential. The authors have reported thickening of films in the prepassive region during anodic polarization and then thinning of the films on attaining passivity. It has been observed that the film thickness on alloy surfaces at open circuit potential is inversely related to the corrosivity of the solution *i.e.* film thickness decreases as the corrosivity of the solution decreases. Film thicknesses in the above investigation have been determined by AES depth profiling technique, the discussion of which is outside the scope of this paper.

*2.1a Studies conducted in BARC* Correlation between the corrosion behaviour and composition of the oxide film formed on carbon steel in 10.5 pH lithium hydroxide solution has been established. Carbon steel, when exposed to deaerated 10.5 pH lithium hydroxide solution at room temperature showed negligible corrosion rate. The film formed after 24 hours was examined by XPS. The studies in this section and elsewhere reported in the paper were carried out using PHI model 551 electron spectrometer with  $MgK_{\alpha}$  source. The instrument was calibrated with respect to Au  $4f_{7/2}$  peak at 83.8 eV. C 1s peak at 285.0 eV due to hydrocarbon contamination was used to account for the charging effects. High resolution spectra were recorded using PDP-11/04 computer interfaced with the system. Chemical states of the metal cations in the surface oxide films were determined by comparing positions, shapes and shifts of the peaks of different elements with those of the standard spectra. In Fe 2p spectrum (figure 1), Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  peak maxima occurred at 710.8 eV and 725.1 eV (after correction for surface charging). Fe  $2p_{3/2}$  peak for  $Fe_2O_3$  has been reported to shift towards higher binding energy by 4.2 eV (Gimzowski *et al* 1977; Yin *et al* 1972) with respect to pure metal (706.8 eV) while a shift of 3.0 eV has been estimated for  $Fe_3O_4$  (Ertl and Wandelt 1975; Coad and Cunningham 1974). Kishi and Ikeda (1973) during oxidation studies of iron observed a maximum shift of 4.0 eV.

Allen *et al* (1974) have reported Fe  $2p_{3/2}$  peaks for  $\alpha$ - $Fe_2O_3$  and  $\alpha$ -FeOOH to appear at 711.4 and 711.0 eV respectively while Asami *et al* (1977) report the Fe  $2p_{3/2}$  peak for  $\alpha$ - $Fe_2O_3$  at 710.97 eV, for  $\alpha$ -FeOOH at 711.44 eV and for  $\gamma$ -FeOOH at 711.60 eV. McIntyre and Zetaruk (1977) report the values of  $711.0 \pm 0.15$  eV for  $\alpha$ - and  $\gamma$ - $Fe_2O_3$  and  $711.9 \pm 0.2$  eV for  $\alpha$ -FeOOH. On the basis of these reports, it can be concluded that



**Figure 1.** Fe 2p spectrum for carbon steel exposed to deaerated 10.5 pH lithium hydroxide solution.

a shift of 4.0 eV observed by us of the Fe  $3p_{3/2}$  peak with respect to pure metal indicates iron to be in Fe (III) state.

Figure 2 shows the O 1s spectrum which appears to consist of two peaks of comparable intensities. The peak at 530.0 eV arises as a result of metal-oxygen bond (hereafter will be referred to as OM peak) and that at 531.6 eV arises as a result of metal-hydroxide bonds (referred to as OH peak later in the text). Asami *et al* (1977) have reported OM and OH peaks for  $\alpha$ - and  $\gamma$ -FeOOH at 530.1 eV and at 531.4 eV respectively while McIntyre *et al* (1977) report OM peak for  $\alpha$ -FeOOH at  $530.3 \pm 0.2$  eV and OH peak at  $531.4 \pm 0.2$  eV. On the basis of these reports, it can be concluded that the oxide film formed in this investigation consists of FeOOH, which protects carbon steel from corrosion in deaerated 10.5 pH lithium hydroxide solution. However, it is difficult to say whether FeOOH formed on the surface is in  $\alpha$  or  $\gamma$  form.

## 2.2 Inhibition studies

Inhibition studies using xps have mainly been reported on copper, iron and nickel. Lewis and Fox (1978) estimated the thickness of inhibitive films formed on copper surfaces immersed in solutions of benzotriazole (BTA) by three methods based on xps and compared with the results obtained using a fourth method *viz* electrical capacitance of the films. The methods based on xps involve (a) measurements of the rate of removal of the film by argon ion sputtering, (b) observation of the attenuation of the substrate Cu 2p photoelectron signal on passing through the protective film and (c) a calculation of film thickness from measurements of the intensity of N 1s photoelectron signal from the surface film.

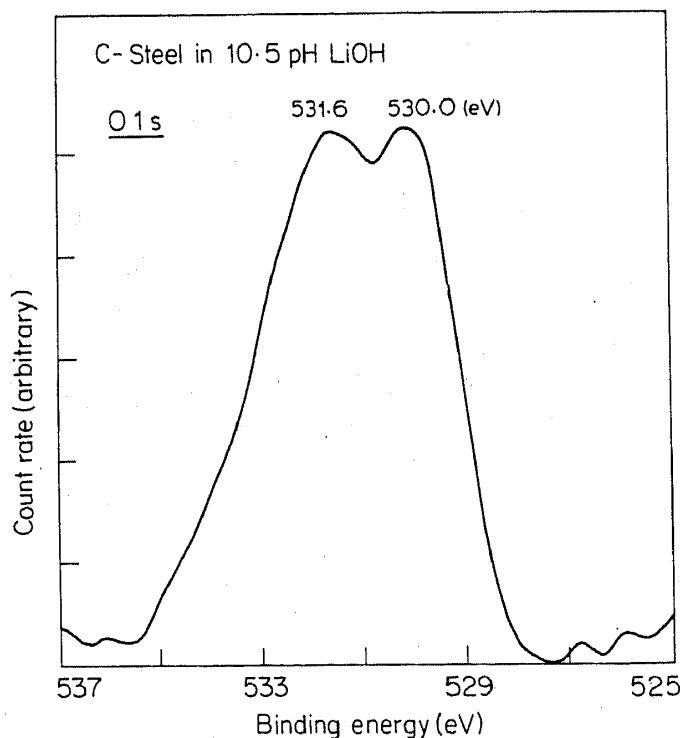


Figure 2. O 1s spectrum for carbon steel exposed to deaerated 10.5 pH lithium hydroxide solution.

In procedure (a), the authors have used the expression

$$J. S. t/\rho = I. S. t/A. e. \rho, \quad (2)$$

for the removal rate of surface molecules by argon ion sputtering where  $J$  is the ion flux,  $I$  is the current,  $S$  is the sputtering yield (*i.e.* the number of surface molecules removed per incident argon ion),  $A$  is the total area bombarded,  $e$  is the electronic charge,  $\rho$  is the density of molecules in surface and  $t$  is the thickness of a monolayer. The accuracy of this method depends upon the value of  $S$ . In the absence of measured values for this quantity, the direct comparison of heats of sublimation of two materials for at least one of which  $S$  is known, would give a satisfactory estimate for the other. Method (b) employed earlier by Carlson and McGuire (1972) is useful when the film and substrate contain a common element, as is the case for all oxide films formed in corrosion processes. Photoelectron intensity from the substrate is assumed to decrease exponentially with thickness of overlying film, then

$$I_s = I_s^0 \exp(-d/\lambda \sin \theta), \quad (3)$$

for electrons emerging at an angle  $\theta$  from the surface.  $I_s^0$  is the intensity without the film,  $d$  is the film thickness and  $\lambda$  is the attenuation length (or mean escape depth) for photoelectrons of a particular energy. In this method, the greatest uncertainties lie in assuming that the dynamics of photoemission and emergence of the electrons produced are similar in all materials used in making the measurements. In method (c) the authors have made use of the fact that nitrogen was such an element which occurred only in the film. The absolute intensity of photoelectrons emitted from N atoms has therefore been correlated with the film thickness. The authors claim to have achieved close agreement between the values obtained by these three methods for determining the film thickness.

Surface films formed by two structurally related corrosion inhibitors *viz* 2-mercapto benzothiazole (MBT) and 2-mercapto benzimidazole (MBIA), on copper studied by xps and x-ray induced Auger spectroscopy have been reported by Chadwick and Hashemi (1979). In this work the films were formed in 0–0.5 NaCl solutions of pH 2–7 on two types of copper samples—one mechanically polished with a thin  $\text{Cu}_2\text{O}$  film and the other with thick  $\text{Cu}_2\text{O}$  film grown electrochemically in KOH. The presence of MBT was established by S 2p and N 1s peaks in the xps spectra. The measured Cu 2p binding energies and the lack of Cu 2p shake-up satellites in the spectra represented copper to be either in Cu(O) or Cu(I) state. The presence of MBT on copper surface did not prove that there was compound formation involving copper, and this evidence was obtained by features of  $\text{CuL}_3\text{M}_{4,5}\text{M}_{4,5}$  Auger peak. According to the mechanism proposed for film formation,  $\text{Cu}_2\text{O}$  first dissolves in acid conditions followed by precipitation of Cu-inhibitor complex on to the metal surface, the thickness of the inhibitor film being low on the copper sample with thin  $\text{Cu}_2\text{O}$  film. It has therefore been suggested that Cu ions originating from the  $\text{Cu}_2\text{O}$  dissolution are involved in the precipitation process. The authors have supported this suggestion by further experimental evidence. Other important studies on inhibitor films which may be of interest to the readers have been reported by Wood and Vannerberg (1978) and Kishi *et al* (1979).

**2.2a Studies conducted at BARC on Cu-10 Ni alloy** The corrosion rate of pure copper in synthetic sea water was 12.4 mdd while that of Cu-10Ni alloy was found to be 3.2 mdd. Ni alloy when exposed to synthetic sea water polluted with 40 ppm sodium sulphide corroded at a rate of 5.1 mdd. All these rates were evaluated on the basis of 15 days

exposure. XPS investigation on these samples were carried out to find out the reason for the decrease in corrosion rate of copper on alloying with nickel and for the increase in the corrosion rate of this alloy in polluted sea water as compared to that in unpolluted sea water.

The film formed on pure copper in synthetic sea water was found to be  $\text{Cu}_2\text{O}$  in accordance with the observation of other workers (North and Pryor 1970; Popplewell *et al* 1973; Kato *et al* 1980). XPS survey scan for Cu-10Ni alloy exposed to unpolluted synthetic sea water (figure 3) indicated that main elements in the film were Cu, O, C and traces of Cl. High resolution Cu 2p spectrum (figure 4) showed no satellites, with  $2p_{3/2}$  peak appearing at 932.7 eV and  $2p_{1/2}$  peak at 952.6 eV. LMM Auger peak maximum for copper (figure 5) occurred at a kinetic energy of 916.6 eV. O 1s peak was asymmetric with a maximum at 530.7 eV (figure 6) and with two higher binding energy shoulders *e.g.* at ca 533 eV and ca 535 eV. No appreciable signal from nickel was obtained from the outermost film.

It is now established that the shake-up satellite structure is closely related to the oxidation state of copper (Larson 1974; Evans 1975; Rosencwaig and Wertheim 1973; Frost *et al* 1972; McIntyre and Cook 1975). All cupric compounds whose Cu 2p spectra have been studied show satellite peaks believed to arise due to multi-electron excitation process whereas Cu 2p spectra of cuprous compounds do not show satellites. Satellites observed by Novakov (1971), Novakov and Prins (1971) and Schoen (1973) in cuprous compounds could be due to surface contamination by cupric species as the cuprous compounds are susceptible to atmospheric oxidation into cupric (Roberts 1974).

Wallbank *et al* (1973) suggested with evidence that satellites originate in 2p spectrum from simultaneous transition to 3d states and if 3d states are fully occupied (as in cuprous species), transition to them are not possible. On the basis of the above

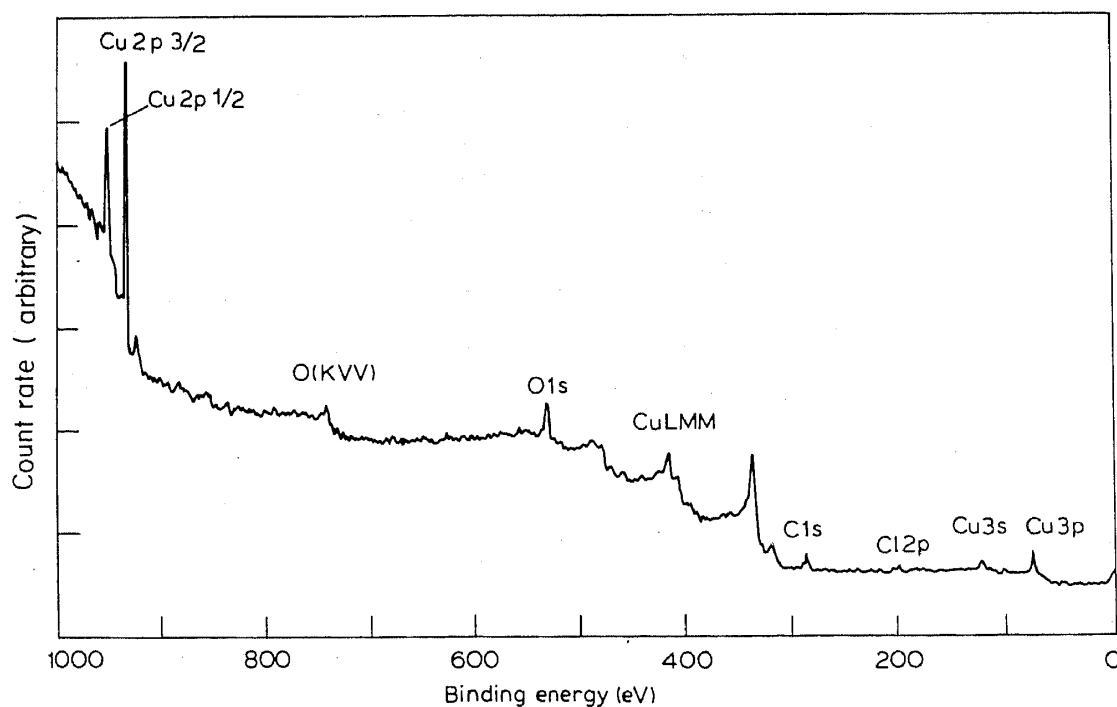


Figure 3. XPS survey for Cu-10Ni alloy exposed to synthetic sea water for 15 days.

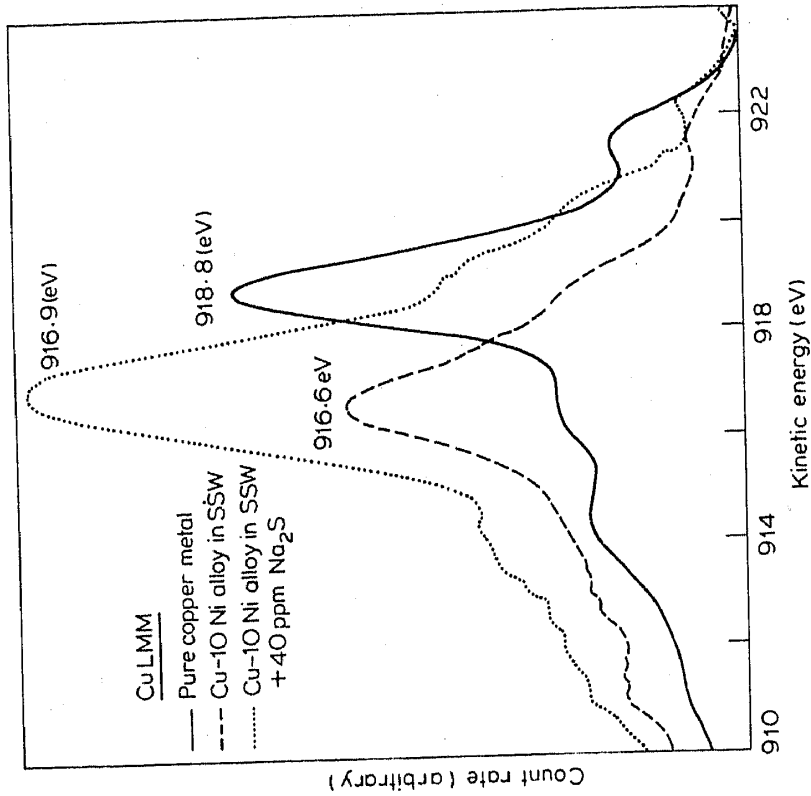


Figure 5. Cu LMM Auger spectrum for pure copper and Cu-10 Ni alloy exposed to synthetic sea water; synthetic sea water + 40 ppm, Na<sub>2</sub>S for 15 days.

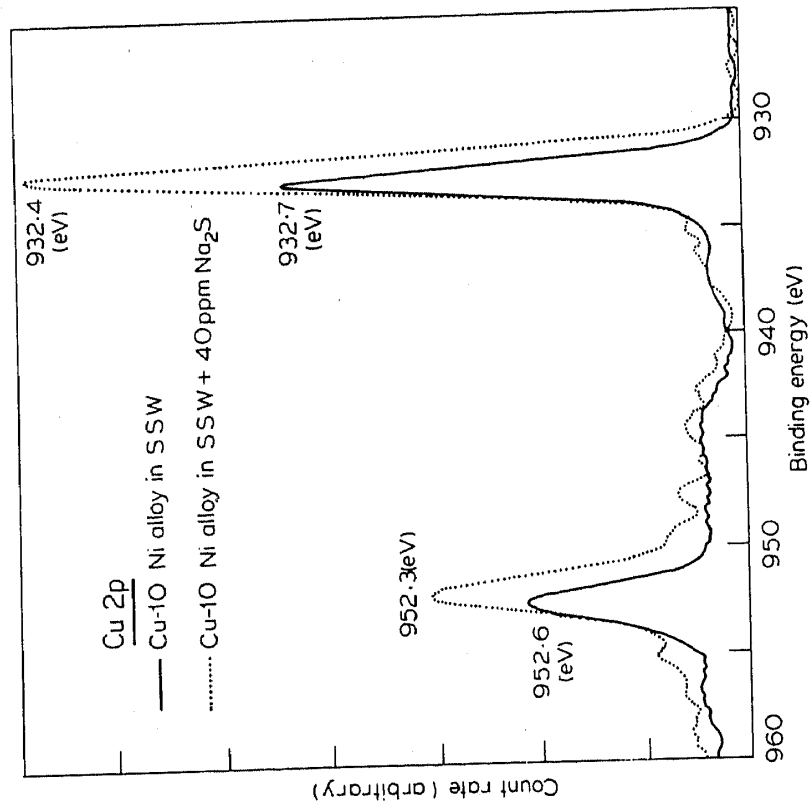


Figure 4. Cu 2p spectrum for Cu-10 Ni alloy exposed to synthetic sea water, and synthetic sea water + 40 ppm Na<sub>2</sub>S for 15 days.



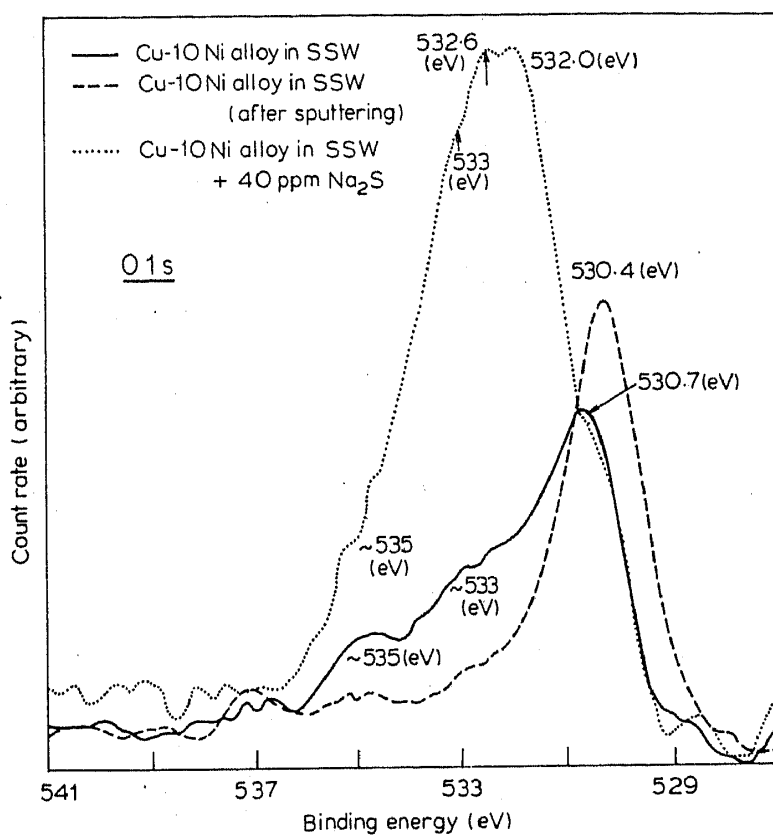


Figure 6. O 1s spectrum for Cu-10 Ni alloy exposed to synthetic sea water; synthetic sea water after sputtering; and synthetic sea water + 40 ppm  $\text{Na}_2\text{S}$  for 15 days.

discussion it can be concluded that copper in this film is not in cupric state. LMM Auger peak at a kinetic energy of 916.6 eV which is quite different from that for pure copper (at 918.8 eV) confirms the presence of cuprous state (McIntyre *et al* 1976). O 1s peak at 530.7 eV can be attributed to the oxide oxygen in  $\text{Cu}_2\text{O}$  (McIntyre *et al* 1976; Evans 1975). Higher binding energy shoulders are due to hydroxide and molecular water which disappear on sputtering. The difference between the binding energies of Cu  $2p_{3/2}$  and O 1s peaks is 402.0 eV which agrees well with the values reported for  $\text{Cu}_2\text{O}$  (Evans 1975). Hence, outermost corrosion film in this case can be concluded to consist of  $\text{Cu}_2\text{O}$  with traces of chlorine in the film.

There was no significant change in copper spectrum on sputtering, but additional nickel signal was obtained. Ni  $2p_{3/2}$  peak showed two maxima *e.g.* at 854.5 eV and at 856.4 eV. There was a shoulder at *ca* 852.8 eV and shake-up satellite structure at *ca* 861 eV and at *ca* 864 eV (figure 7). xps investigations of nickel-oxygen system reveal a shift of 1.6 eV for Ni  $2p_{3/2}$  peak in NiO with respect to that for pure metal (McIntyre *et al* 1976; Kim *et al* 1974; Brundle 1975; Allen *et al* 1979). The peak at 854.5 eV and a satellite at *ca* 861 eV agree well with the results of Kim *et al* (1974) for NiO but the peak at 856.4 eV is too intense to be confused as multiplet splitting of the peak at 854.5 eV (McIntyre and Cook 1975; Kim and Winograd 1974; Kim *et al* 1974). It appears that the peak at 856.4 eV and the satellite at *ca.* 864 eV occur as a result of higher oxidation state of nickel. O 1s peak after sputtering became symmetric and the maximum occurred at 530.4 eV which is not unexpected because the major portion of the film still consisted of

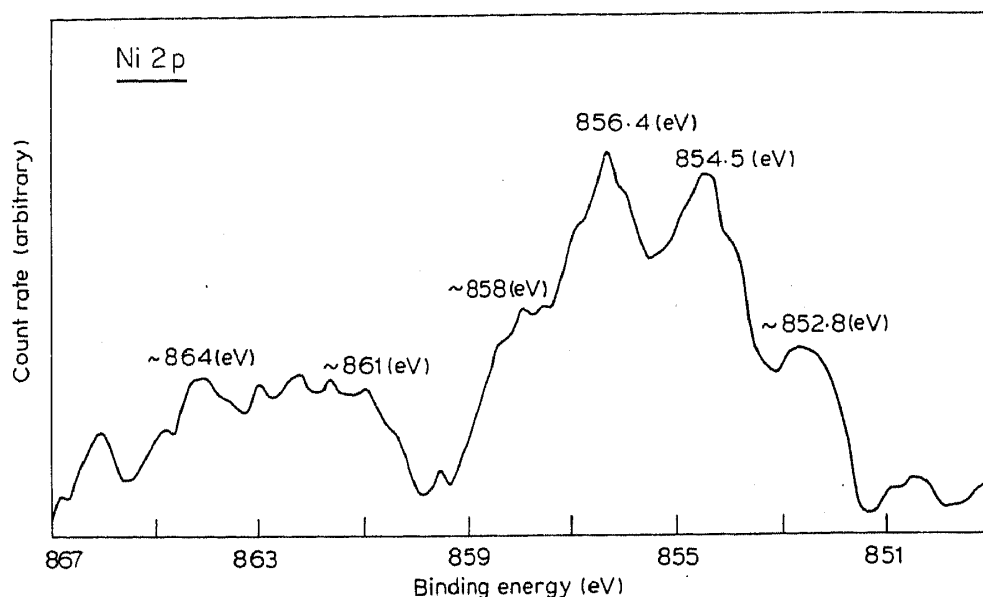
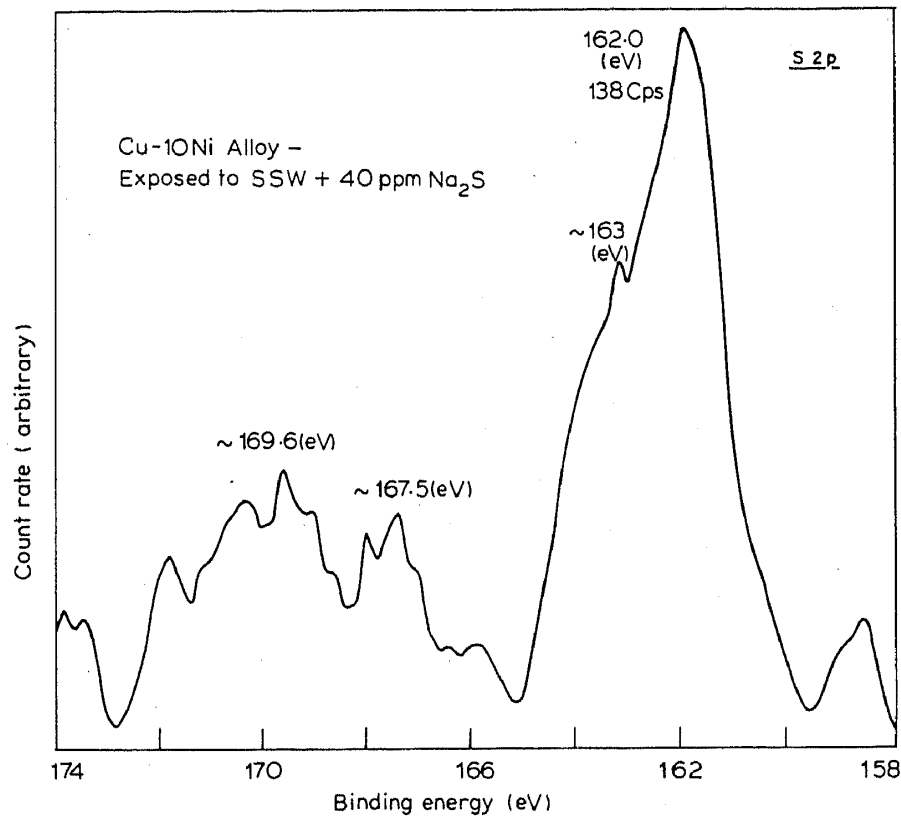


Figure 7. Ni 2p spectrum for Cu-10 Ni alloy exposed to synthetic sea water for 15 days after sputtering.

$\text{Cu}_2\text{O}$ . Haber *et al* (1976) have reported the binding energy values of O 1s peak associated with  $\text{Ni}^{3+}$  and  $\text{Ni}^{2+}$  as 529.3 eV and 529.8 eV respectively; however, other authors (Kim and Winograd 1974; Brundle 1975; Norton *et al* 1977) report the value associated with  $\text{Ni}^{3+}$  as ca 531.5 eV. It can therefore be concluded that the inner film also consisted mainly of  $\text{Cu}_2\text{O}$  with nickel ions in two different valence states *viz*  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  either as a dopant in  $\text{Cu}_2\text{O}$  film or simultaneously existing as a mixture of NiO and  $\text{Ni}_2\text{O}_3$ , however, the O 1s spectrum does not provide evidence to the presence of separate nickel oxide because of domination of  $\text{Cu}_2\text{O}$  in the corrosion film.

The film formed on copper in synthetic sea water was  $\text{Cu}_2\text{O}$  which is a *p*-type semiconductor while that formed on Cu-10Ni alloy in the same medium was  $\text{Cu}_2\text{O}$  doped with  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$ . Doping by nickel ions leads to an increase in ionic and electronic resistivity and consequently the corrosion rate of the alloy decreases in comparison to that of pure copper (Poplewell 1978).

The film formed on Cu-10Ni alloy in polluted sea water was uniformly black and survey scan indicated the presence of Cu, O, S and C. Cu  $2p_{3/2}$  peak appeared at 932.4 eV (figure 4) while LMM Auger peak occurred at a kinetic energy of 916.9 eV (figure 5) indicating copper to be present in cuprous state. O 1s showed a peak with two maxima *viz* 532.0 eV and 532.6 eV and three shoulders at ca 530.7 eV ca 533 eV and ca 535 eV (figure 6). The peak at 535 eV represented molecular oxygen while that at 532.6 eV and shoulder at ca 533 eV represented oxygen in the water molecules bound to the surface film. The shoulder at ca 530.7 eV occurred due to  $\text{Cu}_2\text{O}$  film on the surface. S 2p peak appeared at 162.0 eV (figure 8) with a higher binding energy shoulder at ca. 163 eV and shake-up satellite structure at ca 167.5 eV and ca 169.6 eV. This peak can be attributed to sulphide species (Lindberg *et al* 1970; Binder 1973). Thus, the corrosion product in this case was a mixture of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{S}$  with adsorbed water molecules and oxygen.  $\text{Cu}_2\text{S}$  is known to be a more defective structure than  $\text{Cu}_2\text{O}$ , and  $\text{Cu}_2\text{O}/\text{Cu}_2\text{S}$  corrosion product film is much more defective than  $\text{Cu}_2\text{O}$  alone, thus resulting in an increased ionic and electronic transport through the film (Bates and



**Figure 8.** S 2p spectrum for Cu-10 Ni alloy exposed to synthetic sea water + 40 ppm Na<sub>2</sub>S for 15 days.

Popplewell 1975). The resultant crystals will have a mismatch at interfaces that would result in structural defects large enough to permit the mass transport of moisture with dissolved molecular and ionic species. Such a porous structure is responsible for the increase in corrosion rate in polluted sea water.

### 2.3 Pitting studies

Sugimoto and Sawada (1977) have studied the effect of molybdenum additions to stainless steels in inhibiting pitting in acid chloride solutions. Solution annealed austenitic 20Cr-25Ni steels containing 0-5 wt % Mo were polarised in deaerated 1N HCl (pH 0.02) in steps of 25 mV from the corrosion potential and xps investigations were carried out at different stages of polarization. Anodic polarization of pure Fe, Cr, Ni and Mo showed that Fe and Ni did not passivate and MO exhibited transpassive anodic dissolution above -0.03 V and consisted a film of MoO<sub>3</sub> above -0.03 V. Anodic polarization of Fe-Cr alloys containing 15-70 wt % Cr indicated no pitting in the alloys containing > 40 wt % Cr. On alloying with 5 wt % Mo the amount of Cr needed to inhibit pitting was reduced to half of those without Mo. xps investigations on the passive film formed on 20 Cr-25 Ni-5 Mo steels showed the film to be an oxyhydroxide which contained Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup> and Mo<sup>6+</sup> as cations. The authors have concluded that Cr<sup>3+</sup> and Mo<sup>6+</sup> play a very important role in improving the corrosion resistance of the films. The formation of very compact surface films of CrOOH containing cations like Mo<sup>6+</sup>, Fe<sup>3+</sup> and Ni<sup>2+</sup> has been concluded to be the reason for increase in pitting resistance of Cr-Ni steels on addition of Mo.

#### 2.4 Studies on sacrificial anodes for cathodic protection

Studies on the xps investigations on aluminium sacrificial anodes have been carried out in authors' laboratory and have been reported in detail elsewhere (Pai *et al* 1982). Pure aluminium is not recommended for sacrificial anodes because of passive oxide film on its surface. Judicious additions of Zn, Mg, Cd, Hg, Sn and In as alloying elements can possibly modify this oxide film on aluminium and render Al anodes suitable for cathodic protection of steel structures in sea water.

In this investigation, studies were carried out on Al-5Zn-X Sn alloys where X varied from 0.67% to 0.5%. Current efficiencies (%) of alloys with different heat treatments were measured after coupling to mild steel in sea water for 180 hr. Alloy Al-5Zn-0.1 Sn (heated for 3 hours at 300°C and water quenched) was found to behave best as a sacrificial anode while the same alloy after heating for 3 hr at 300°C and furnace cooling, was not found to be so good. On exposing these specimens to sea water, xps studies indicated that the film formed on the quenched alloy contained, in addition to Al<sub>2</sub>O<sub>3</sub>, relatively greater amount of ZnO than that formed on the furnace cooled alloy. In the oxide layer where ZnO and Al<sub>2</sub>O<sub>3</sub>.3H<sub>2</sub>O are formed, Al<sup>3+</sup> (ionic radius 0.51 Å) ions act as dopant in ZnO film (ionic radius of Zn<sup>2+</sup> 0.93 Å) and increase the cation vacancy concentration. The higher oxygen potential gradient developed due to reduced aluminium activity favours the higher rate of dissolution of Al alloy in sea water by providing driving force for the movement of cations from alloy-oxide interface. Obviously, the quenched alloy in which the amount of ZnO formed is more, will behave as a better sacrificial anode.

### 3. Conclusions

From the above illustrations, it can be seen that xps is a very powerful technique for understanding and solving the corrosion problems. It has been clearly demonstrated that xps can be used for determining the nature, thickness and composition of passive films, for inhibition and pitting studies and for understanding the phenomenon occurring in the cathodic protection. The authors' studies indicate that formation of FeOOH provides protection to carbon steel against corrosion in deaerated alkaline medium, better corrosion resistance of Cu-Ni alloys in sea water is due to the formation of Cu<sub>2</sub>O film doped with Ni<sup>2+</sup> and Ni<sup>3+</sup>, the enhancement of corrosion of these alloys in sulphide polluted sea water occurs due to the formation of porous corrosion product Cu<sub>2</sub>O/Cu<sub>2</sub>S and sacrificial aluminium-zinc-tin alloy anodes behave better when the oxide film is rich in zinc.

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