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Electrochemical and surface analytical study of the formation of oxide films on monel-400 and copper in alkaline media

Abstract The nature of the oxide films formed on monel-400 and copper in presence of NaOH and *N*-methylpyrrolidine (a volatile amine) at pH 9.5 and in 0.1 M KNO_3 medium were investigated. The oxide films were grown by applying an anodic potential of $+0.4$ V (vs saturated calomel electrode) for 30 min. The compositions of the surface oxide films were analysed by X-ray photoelectron spectroscopy. In the case of copper in NaOH medium, Cu(0) and a very small amount of copper hydroxide were observed. However, in amine medium, Cu(0) and Cu-amine complex were found. For monel in NaOH, the anodic film was found to contain hydroxides of both copper and nickel. After sputtering, this film showed a small amount of metal oxide below the hydroxide layer as confirmed by the oxygen peak. In amine medium the anodic film was found to contain only nickel hydroxide and metallic copper. The depth profile analysis of films showed that the film developed was very thin and the nickel hydroxide was sputtered very easily from the film.

Key words Monel · Copper · Steam-generator · *N*-methylpyrrolidine · X-ray photoelectron spectroscopy

Introduction

The steam generator (SG)/boiler circuit of a nuclear power plant assumes importance as it forms the pressure boundary between the primary radioactive coolant and

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the secondary non-radioactive water. Any corrosion damage to the SG tubing can result in spreading of radioactivity to the secondary system and leakage of costly heavy water in the case of pressurised heavy water reactors (PHWRs). In addition, fouling and scaling of SG tubes could result in decreased heat transfer efficiency resulting in turn in reduced power production. The corrosion behaviour of nuclear steam generator tube materials is controlled by the water chemistry of the aqueous environment, which determines the nature of the passive oxide films and metal ion transport in the coolant circuit.

Of the various water chemistry parameters, pH is one of the most important, and should be monitored and controlled in order to minimise the corrosion damage to the SG tubes and hence to preserve their integrity. The pH control in the SG/feed water circuit is mainly carried out by a procedure known as 'all volatile treatment' (AVT), wherein a volatile chemical is added to the feed water to maintain a pH of 8.5–9.5. Organic amines such as ammonia, morpholine, cyclohexylamine etc. are generally used for this purpose as they not only hydrolyse to give the required pH range but also volatilise and condense with the first droplet of the condensate so as to give protection to the entire steam-water circuit. These amines are good complexing agents and hence affect the nature of the oxide films formed on the SG tube surfaces.

Copper alloys have been used for sea water as well as fresh water cooled condensers and heat exchangers because of their good heat transfer properties, relatively low cost and high resistance to corrosion. However, copper-related problems in various forms have been encountered in many nuclear and fossil-fuelled installations. For example, in boiling water reactors (BWRs), crud-induced localised corrosion (CILC) of fuel rods was observed [1] due to the interaction between a tenacious scale of copper-rich oxide crud and nodular zirconium oxide deposits formed on cladding surfaces. In pressurised water reactors (PWRs), copper has been implicated to some degree in problems like pitting under

sludge piles, denting at tube supports and intergranular attack or stress corrosion cracking (IGA-SCC) in the SG circuits [2]. It has been observed that 70/30 Cu/Ni is de-nickelising on both tube and shell sides of the high-pressure heaters and that the copper remaining flakes off [3]. Notwithstanding the above problems, copper alloys have been used world over for the SG/feed-water circuits and some Indian PHWRs are no exception.

Various surface analytical methods such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) have been applied to understand the corrosion phenomena and to get an insight into the chemical structure of the surface films formed by passivation [4–5]. A detailed study of the quantitative surface analysis of the passive films developed on Ni-Cu alloy in an NaOH alkaline medium was given by Peter Druska et al. [6] where a multi-layer structure of the film was assumed. In the present work, the nature of the oxide films formed on monel-400 and copper in the presence of NaOH and N-methylpyrrolidine (a volatile amine) at pH 9.5 and in 0.1 M KNO3 medium were investigated.

Experimental

The specimen surfaces were polished with 600 grit emery paper followed by diamond paste, ultrasonically cleaned in distilled water and dried in air. A cathodic reduction at a current density of 5 mA/cm^2 was performed (5 min) to remove the air-oxidised films, and the corrosion potential was measured after a few minutes. The coupons were polarised at +0.4 V vs SCE for 30 min in the appropriate electrolytes, removed under applied potential, rinsed with water and dried in an argon atmosphere. The composition of the surface oxide films was analysed by XPS. For electrochemical application, the 1286 Electrochemical Interface (Solartron, USA) was used. The surface analytical studies were done with an ESCALAB 200× spectrometer (VG Scientific, UK) equipped with a hemispherical analyser whose plates are separated by a 20-eV voltage difference for data acquisition. An Al-Kα X-ray source was used for excitation.

Results and discussion

Electrochemical analysis

Figure 1 shows the potentiodynamic polarisation curves for monel and copper in N-methylpyrrolidine (amine) and NaOH at pH 9.5. As can be seen, the corrosion potentials (E_{corr}) of both monel and copper shift to more noble values in the presence of NaOH. In the case of copper, the anodic polarisation curves showed a shoulder around 0.0 V (vs SCE) which was prominent in the amine medium. This could be due to some unprotective film formation or localised corrosion attack like pitting. The corrosion current density (I_{corr}) in the amine medium was found to be higher than in NaOH medium because of the formation of soluble copper-amine complexes. In case of monel, a shoulder appeared around 0.2 V (vs SCE) only in NaOH medium. However, microscopic examination did not show any pit
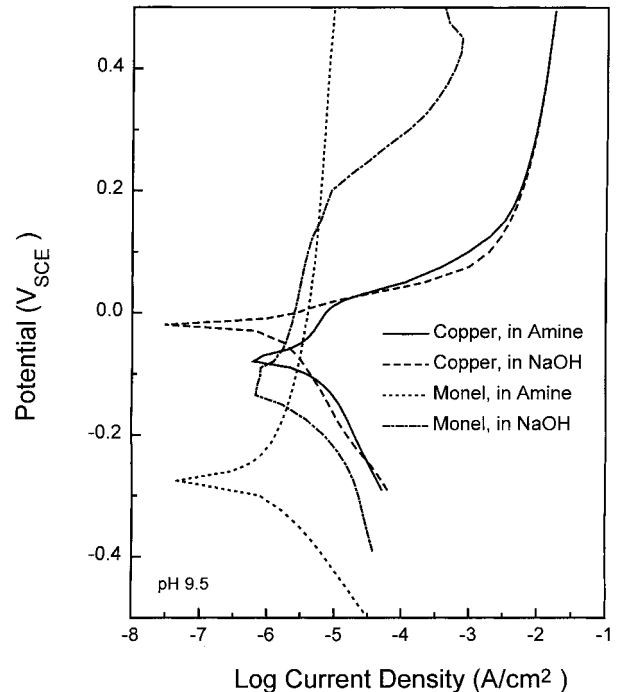

Fig. 1 Potentiodynamic polarisation curves for monel and copper in NaOH and N-methylpyrrolidine at pH 9.5

formation on either material. Since a surface film was observed on the coupons at the end of the experiments, the films were developed in the mass-transfer-controlled potential region (+0.4 V vs SCE) for comparison.

XPS analysis

Copper

The binding energy of Cu 2p$_{3/2}$ level from pure metal was observed at 931.9 eV, with an FWHM (full width at half maximum) of 1.9 eV. Subsequent to the electrochemical treatment of Cu in NaOH medium, the XPS spectra for Cu showed two peaks for 2p$_{3/2}$, as given in Fig. 2. The most prominent peak, observed at 931.9 eV with a slightly larger FWHM (2.1 eV), corresponded to unoxidised Cu, and this could be from the base metal either because of thinness or non-homogeneity of the film. The second peak, which appeared as a shoulder at higher binding energy, namely 933.7 eV (arrow), showed the chemical shift of 1.8 eV, which indicated the formation of hydroxide on the surface [6]. The hydroxide formation was further confirmed by O 1s peak analysis, which is presented later. From the intensity of the shoulder, it is clear that the concentration of Cu^{2+} was extremely small.

Copper metal subjected to the electrochemical treatment in N-methylpyrrolidine medium showed only one peak for Cu 2p$_{3/2}$ at binding energy 932.7 eV with 2.1 eV FWHM. This binding energy showed the presence of the +1 oxidation state of Cu, e.g. Cu_2O [6]. However, in
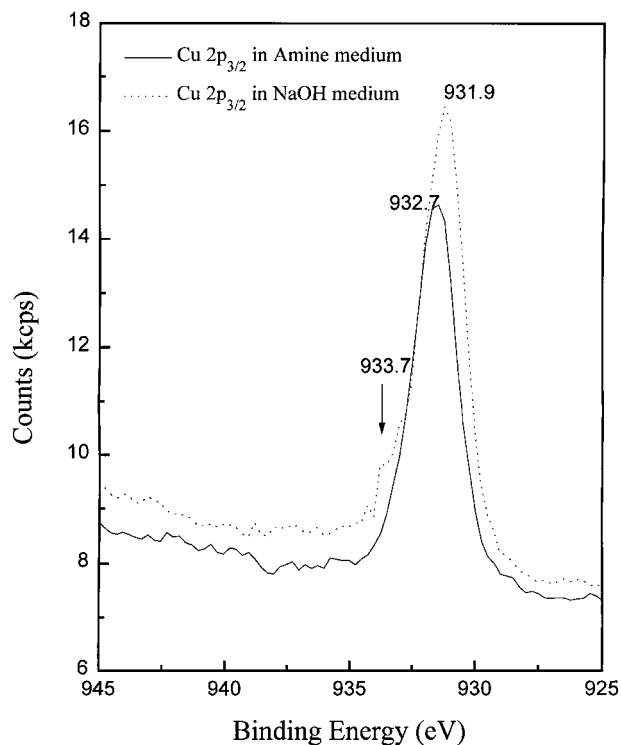
Fig. 2 XPS signals of Cu $2p_{3/2}$ passivated in NaOH and N-methyl-pyrrolidine at pH 9.5

Fig. 3 XPS signals of Cu $2p_{3/2}$ in monel passivated in NaOH and N-methylpyrrolidine at pH 9.5

general Cu $2p_{3/2}$ from Cu_2O is associated with some satellite at around 943 eV due to the source X-ray [6], but this was not observed in our work. Similarly, the FWHM of the peak observed was 2.1 eV, which was around 0.8 eV less than that observed for pure Cu_2O taken with the same instrument. Schon [7] has reported 4.5 eV FWHM for Cu_2O. Hence it was surmised that the Cu(+ 1) state observed in this work might not be Cu_2O but some other Cu(+ 1) compound.

An XPS signal corresponding to nitrogen was detected in the sample of Cu exposed to the amine. Hence it was presumed that a Cu(I)-nitrogen complex might be present. The Cu was not present in the + 2 state because the usual higher energy satellite peaks were not observed. The N 1s peak was observed at 399.2 eV and the C 1s peak at 284.6 eV with tailing at the high binding energy side. Thus, in the process of oxidation of Cu in the presence of N-methylpyrrolidine, a Cu(I)-nitrogen complex was formed on the surface. After sputtering, the nitrogen peak vanished completely, but a trace of C was observed to be still present, of course with the tailing at the higher binding side of the peak.

Copper in monel

The passive film developed on the monel was distinctly different from that developed on Cu. Figure 3 shows the XPS signals for the Cu $2p_{3/2}$ peak from monel in both media. In the case of monel in NaOH medium, the Cu $2p_{3/2}$ peak was observed at 933.7 eV with a distinct
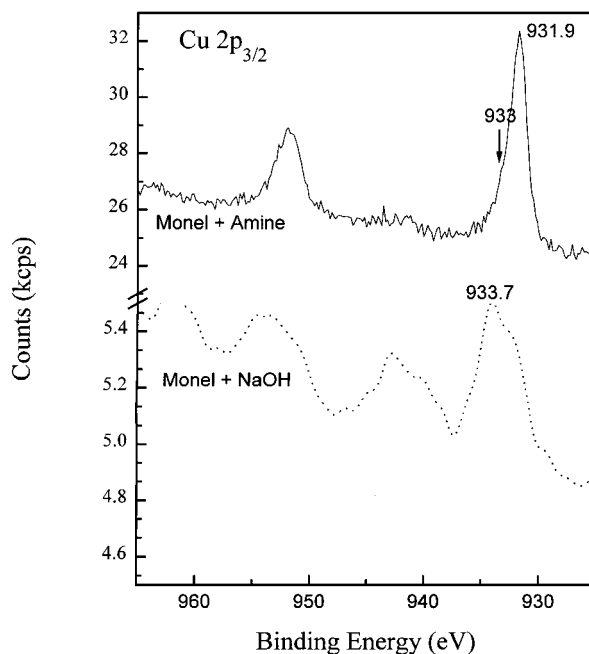
broad satellite peak at around 944 eV. Not only the chemical shift of Cu $2p_{3/2}$ but also the peak shape with the shoulder at lower binding energy (931.9 eV) indicated the formation of copper hydroxide [6]. The shoulder associated with the fingerprint of Cu $2p_{3/2}$ in $Cu(OH)_2$ is due to the X-ray effect which decomposes hydroxide to Cu(0) [8]. The broadness of the satellite peak indicated two different types of shake-up transitions characteristic of the compound [6]. In comparison to pure Cu metal, the formation of $Cu(OH)_2$ was found to be more on monel in the presence of NaOH.

Though in situ sputtering is a widely used technique for depth profiling of thin films, in the case of films of a Cu compound this method is not suitable because most of the Cu(II) compounds undergo decomposition in X-ray [8] and Ar ion beams [9]. The major decomposition products are cuprous compounds or pure Cu [10, 11]. However, $Ni(OH)_2$ does not undergo such dissociation in the Ar ion beam [9]. The hydroxide film developed on monel in NaOH medium on sputtering showed the oxides of Cu and Ni. Because of the above sputtering effect on copper compounds, it is difficult to characterise the layer structure and model the mechanism of film growth.

In the case of N-methylpyrrolidine medium, Cu in monel was not very intensely oxidised. The prominent peak was observed at 931.9 eV, which could be from the base alloy. The peak shoulder at around 933 eV (Fig. 3) could possibly be due to the formation of some Cu(I)-nitrogen complex as in the case of pure metallic Cu.
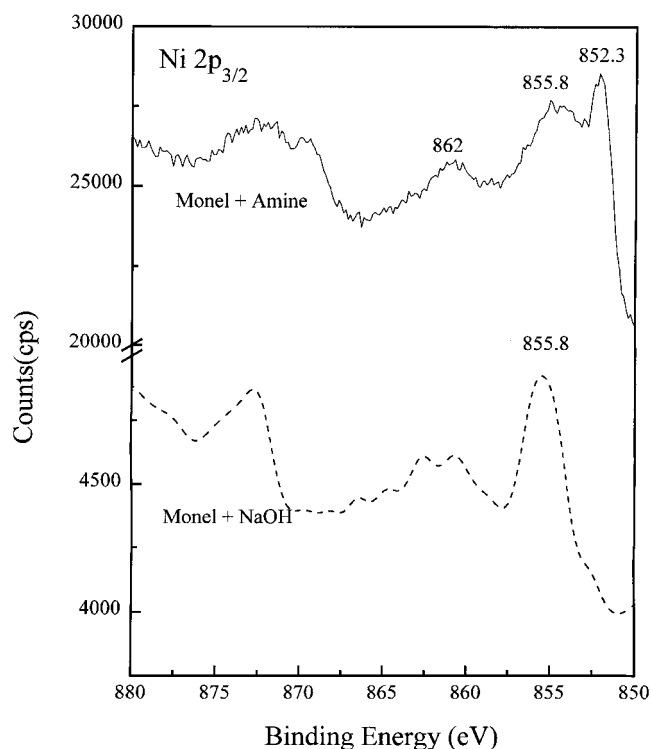
The N 1s and C 1s peaks were observed at 399.5 eV and 284.6 eV respectively, with a tailing at higher binding energy for C. The Cu in amine and Cu(monel) in amine showed identical peaks for carbon.

Nickel in monel

Pure Ni showed a 2p$_{3/2}$ peak at 852.3 eV with an FWHM of 2.0 eV. Monel oxidised in NaOH medium showed only one peak for Ni 2p$_{3/2}$ at 855.8 eV with 3.5 eV FWHM which corresponded to Ni(OH)$_2$. Figure 4 shows the XPS signal for the Ni 2p$_{3/2}$ peak from monel in NaOH medium. The chemical shift observed in this case was 3.5 eV, which was close to the value of 3.1 ± 0.3 eV quoted by McIntyre et al. [10]. The broad satellite at around 862 eV confirmed the presence of hydroxide on the surface [10]. In NaOH, Ni oxidation to Ni(OH)$_2$ occurred predominantly, and the film was thick enough to cover the Ni(0) signal from the base monel alloy.

Monel oxidised in *N*-methylpyrrolidine medium showed two 2p$_{3/2}$ peaks of binding energy 852.3 eV and 855.8 eV with a broad satellite at 862 eV. Though the presence of Ni(OH)$_2$ was confirmed, some Ni(0) was also seen.

Assuming the layer-by-layer growth [6] of the film, Cu(0) and Ni(0) signals from monel were seen after pasivation. It is known that the intensity of the photoemission peak exponentially decays with the depth of emission and vanishes at the escape depth of the electron [12]. Hence the presence of Cu(0) and Ni(0) signal in the surface of monel conditioned in amine medium implies that the thickness of the film was of the order of magnitude of the mean free path of the Ni 2p$_{3/2}$ photoelectrons.

Oxygen

O 1s peaks in the four cases are shown in Fig. 5. In the case of Cu, the O 1s peak observed at around 532.5 eV in hydroxide or amine media was due to the adsorbed water on the surface [13]. However, in NaOH medium, the O 1s signal from Cu(OH)$_2$ broadened the peak at 532.5 eV.

In the monel case, the O 1s peak appeared at 531.6 eV and 531.7 eV with the FWHM values of 2.2 eV (after fitting) and 3.2 eV for NaOH and amine medium respectively. However, in amine medium, there was a tailing of the O 1s peak at the higher binding energy side. This could be the result of H$_2$O adsorption as mentioned above.

Traces of carbon were observed on all the films as surface contaminant. The carbon intensity was measured in comparison to that of the oxygen present on the surface. The observed ratio for C/O was around 0.2 for all the cases except in the case of monel in NaOH medium where it was less than 0.2. The C 1s peak could have come from the sample preparation/handling procedures even after taking careful precautions.

Conclusions

The results showed that the film compositions differed depending on the medium under which passivation was carried out. The sputtering of films showed that the films developed were very thin. For copper in NaOH medium,

Fig. 4 XPS signals of Ni 2p$_{3/2}$ in monel passivated in NaOH and *N*-methylpyrrolidine at pH 9.5
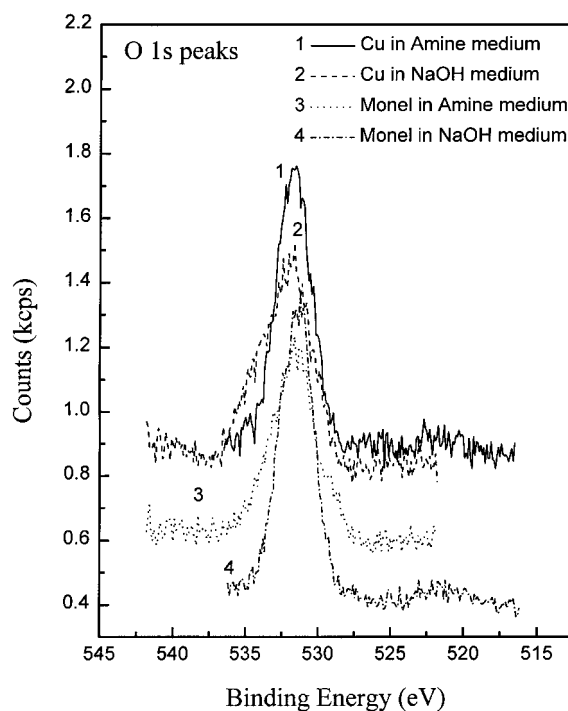
Fig. 5 XPS signals of O 1s in copper and monel passivated in NaOH and *N*-methylpyrrolidine at pH 9.5

Cu(0) and a very small amount of copper hydroxide were observed. In amine medium, Cu(0) and Cu-nitrogen complex were found. For monel in NaOH medium, hydroxides of both Cu(II) and Ni(II) were observed. For monel in amine medium, the anodic film was found to contain predominantly nickel hydroxide.

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