Mott–Schottky analysis of passive films on Cu containing Fe–20Cr–xCu (x=0, 4) alloys

I. H. Toor*1, M. Ejaz2 and H. S. Kwon3

Effect of copper on the defect density of Fe–20Cr–xCu (x=0, 4) stainless steel alloys was investigated in deaerated pH 8.5 borate buffer solution at room temperature using Mott–Schottky analysis. Mott–Schottky analysis revealed that the addition of copper increased the acceptor density (N_A, V_{Cr}^{3-}), i.e. decreased the Cr^{3+} content of the passive film. Also the donor densities, shallow donor (N_{D1}, V_{C}^{+2}) and deep donor (N_{D2}, V_{Cr}^{+6}), of the passive films formed were increased. XPS analysis confirmed the decrease in Cr content and enrichment of copper in the passive film of Cu containing alloys, which ultimately dictated their lower corrosion resistance, i.e. decreased film protectiveness and stability.

Keywords: Fe–Cr alloys, Copper, Semiconducting properties, Passive films, Mott–Schottky analysis, Impedance, Stainless steel, XPS

Introduction

Conventional 300-series austenitic stainless steels (SSs) have been widely used as structural materials in various corrosive environments due to their excellent resistance to corrosion and good mechanical properties. Along with Nickel (Ni) and Chromium (Cr), many other alloying elements such as; Silicon (Si), Copper (Cu), Molybdenum (Mo), Nitrogen (N), Carbon (C) and Tungsten (W), etc., are added in stainless steels depending on their final application requirements. Therefore, there have been needs for developing new austenitic SSs in which expensive Ni is replaced with inexpensive austenite stabilizing elements such as manganese (Mn) and N, etc.1,2

Copper, an austenite former, is also used as a substitute for Ni (like C, N or Mn) in austenitic SSs, even though its austenizing power is relatively weak as compared to C and N. Many researchers reported the use of Cu in ferritic, austenitic and duplex SSs to improve their resistance to uniform corrosion in sulphuric media.3,4 Seo et al.5 pointed out that the presence of 0.4 wt-% Cu decreased the anodic dissolution rate of ferritic stainless steel in sulfuric acid. Ogura et al.6 found that the addition of 0.1–1.0 wt-% of Cu to austenitic stainless steel could also cause a decrease of its corrosion rate in 5 N H2SO4/NaCl solutions. Streicher6 indicated that the addition of Cu (3.5 wt-%) to 20Cr–33Ni–2.5Mo alloy greatly enhanced the resistance of the alloy to sulphuric and phosphoric acid environments. Wilde and Greene7 observed that Cu excels among alloying elements in decreasing the critical anodic current density, which is a criterion to assess the passivation tendency of the alloys in acidic media. Some researchers reported that Cu is enriched on the surface during the anodic dissolution of the alloy and reduce the corrosion rate8,9 in acidic solutions.

It is well established that passive films on SSs are responsible for their excellent corrosion resistance in different environments. Different alloying elements in SSs affect the structure and composition of this thin passive film differently, so understanding the role of individual alloying elements on passive film structure and composition is very important. This structure and composition will ultimately affect the corrosion resistance behavior of SSs and Ni base alloys, so an understanding of the mechanisms involved will be very useful in designing new corrosion resistant SSs. There are many studies which showed that the passive films on SSs consist of Cr enriched (Fe, Cr) oxide/hydroxide,9–14 although there is still some controversy as to the detailed structure and composition of the passive film. The extreme complexity of the metal/passive film/electrolyte system of SSs makes the clarification of the passive film difficult. It is because of the experimental difficulties in probing the thin passive film of few nm thick and also due to the possibility of compositional variation when the film is brought out for ex situ surface analysis.15 Thus ex situ analytical studies for passive film characterisation are not sufficient to reveal the real structure of passive film. Recently, photo electrochemistry and Mott–Schottky analysis have proved to be a powerful technique for in situ analysis of passive films on metals and alloys.15–17 These techniques are based on the fact that passive film acts like a semiconductor, so these techniques enable us to measure the semiconducting properties of the passive films, which are intimately related with the physicochemical structure of the passive film, i.e. to the corrosion properties.

Though there have been few studies on the role of Cu on corrosion resistance properties of SSs, but how Cu

1Department of Mechanical Engineering, King Fahd University of Petroleum & Minerals (KFUPM), Dhahran 31261, Kingdom of Saudi Arabia
2ENGTEQ, Haresh Road, Aberdeen AB12 3LE, UK
3Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1, GuSeongDong, YuSeongGu, DaeJeon, 305-701, Korea
4Corresponding author, email ihsan@kfupm.edu.sa

© 2014 Institute of Materials, Minerals and Mining
Published by Maney on behalf of the Institute
Received 6 September 2013; accepted 13 January 2014
DOI 10.1179/1743278214Y.0000000154

Corrosion Engineering, Science and Technology 2014 vol. 000 no 000 1
affects the passive film defect density and composition was rarely investigated before. Therefore, the objective of this study was to investigate the effect of Cu on the defect density of Fe–20Cr–xCu (x=0, 4) alloys in pH 8.5 borate buffer solution using Mott–Schottky analysis. X-ray photoelectron spectroscopy (XPS) investigations were also carried out on the passive films formed on Fe–20Cr–xCu (x=0, 4) alloys.

**Experimental methods**

Alloys used in this study Fe–20Cr–xCu (x=0, 4) were prepared in vacuum arc melting furnace. The cast was homogenized for 120 min at 1200 °C, and then hot rolled into 3 mm thick plate. Specimens were prepared after cold rolling the hot rolled plates into 1.6 mm thick sheets and solution annealing for 1050 °C for 60 min, followed by water quenching. For electrochemical tests, the specimens were polished to 2000 grit emery paper and then ultrasonically cleaned with distilled water. A three electrode cell composed of a specimen as a working electrode, a Pt counter electrode and a saturated calomel reference electrode was used for the tests. Polarisation tests were carried out at a scan rate of 1 mV s⁻¹ in pH 8.5 borate buffer solution at room temperature (25 °C).

The in-depth chemical composition profile of the passive films formed on Fe–20Cr–xCu (x=4) alloys formed potentiostatically at 0.4 V (SCE) for 24 h was examined using X-ray photoelectron spectroscopy (XPS). XPS measurements were performed using Al Kα and Mg Kα X-ray source (15 kV, 20 mA, 300 W), and a pass energy of 20 eV. The reference energies were the Cls signal at 284.5 eV and the O1s signal at 531.0 eV. Characterisation of the passive films was performed by means of high resolution scan and sputtering depth profiles. Sputter depth profiles were obtained with argon ions (P₆₀=5×10⁻¹⁰ torr, base pressure = 5×10⁻¹⁰ torr, energy: 5 kV, current: 3–0 μA cm⁻²).

For Mott–Schottky analysis, the specimen were passivated at selected film formation potential, Uₐ [0–4–0.8 V(SCE)] for 9 h, before capacitance was measured by sweeping the applied potential at a rate of 1 mV s⁻¹ from the film formation potential to −1.0 V(SCE). The excitation voltage was 10 mV (peak-to-peak) and the frequency was 1 kHz.

**Results and discussion**

**Polarisation tests**

Figure 1 shows the polarisation behaviour of the Fe–20Cr and Fe–20Cr–4Cu alloys in deaerated pH 8.5 borate buffer solution at 25 °C with scan rate of 1 mV s⁻¹. Corrosion potential (Ecorr) of the two alloys was almost equal: −0.65 V(SCE) for Fe–20Cr and −0.6 V(SCE) for Fe–20Cr–4Cu alloy respectively. The first anodic current at −0.57 V(SCE) was ascribed to the anodic dissolution or the oxidation of Fe to Fe²⁺, the current at −0.35 V(SCE) was related to the oxidation of Fe²⁺ to Fe³⁺, and finally the anodic current at 0.72 V(SCE) was related to the transpassive oxidation of Cr³⁺ to Cr⁶⁺. It appears that there is close similarities in the polarisation behaviours between Fe–20Cr alloy and Fe–20Cr–4Cu alloy. Passive current density was slightly higher in the Fe–20Cr–4Cu alloy as compared to Cu free alloy. It is also from Fig. 1 that addition of Cu increased the anodic dissolution of Fe to Fe²⁺ and of Fe²⁺ to Fe³⁺. Based on Fig. 1, 0–4 V(SCE) was chosen as film formation potential (U) for subsequent Mott–Schottky analysis and XPS measurements.

**XPS analysis of passive film**

Fig. 2a and b shows the XPS atomic concentration of the passive films formed at 0–4 V(SCE) on Fe–20Cr and Fe–20Cr–4Cu alloys, for 24 h in deaerated pH 8.5 borate buffer solution at room temperature and Fig. 3 shows the relative concentration of Cr, that is Cr/(Cr + Fe + Cu) [%], Cu and Fe respectively in Fe–20Cr–xCu alloys, calculated from Fig. 2a and b.

In both copper free and copper containing alloys, iron concentration was about 20–30 at-% at the subsurface and increased gradually with depth. The concentration profile of O in both films exhibited peak value of 25–40 at-% at the subsurface, 1 mm depth and then decreased with depth. Slight amount of Cu was also present at the subsurface and it was increased with depth in Cu containing alloy. The Cr atomic ratio of the passive film was decreased in the outer surface from 50% (in Cu free alloys) to less than 40% (in Cu containing alloys), as shown in Figs. 3a and b respectively. Cu was also found enriched in the passive film on Fe–20Cr–4Cu alloys. This result is in a good agreement with the previous results²⁰,²¹ that a small amount of Cu can be enriched in the film and it can decrease the Cr content of the passive film.

Therefore, the XPS analysis results showed that passive film is (Fe, Cr) oxide for Fe–20Cr alloys and for Fe–20Cr–4Cu alloys, it is found to be (Cu+Cr) enriched γ-Fe₂O₃ (as will be discussed in next section of Mott–Schottky analysis). Also the presence of Cu decreased the chrome content of the passive film in Cu containing alloys (Fig. 3b) and this will be further confirmed by Mott–Schottky analysis in the section on ‘Mott–Schottky analysis’, by increased acceptor defect density (N_A, V_Cr⁻³) of the passive film on Cu containing alloys. Therefore, based on these investigations, it is suggested that passive film on Cu containing Ss will be less protective and less stable, due to decreased Cr concentration in the passive film.

It has been reported by researchers⁴,⁸ that Cu is enriched on the surface of Fe–26Cr–0–4Cu alloy.
and Fe–18Cr–8Ni–xCu (x=0–3 wt-%) alloys during the anodic dissolution of these alloys in deaerated sulphuric acid solution and due to this Cu enrichment, corrosion rate of the alloys was decreased in the active region. However in the passive state, results were opposite and Cu showed detrimental effects on the stability of passive films on Fe–26Cr–0.4Cu alloy and Fe–18Cr–8Ni–xCu (x=0–3 wt-%) alloys. In his work, Bautista et al.22 investigated the corrosion resistance behaviour of an alloy 204Cu (Fe–16Cr–2Ni–8Mn–2.7Cu–0.13N), which is used for concrete reinforcements in low alkaline media and reported that the passive layer of 204Cu type SS, is attacked more significantly than that of commercial AISI 304 grade and duplex SAF 2205 grade. In another work, Oguzie et al.23 found the detrimental effect of Cu on the passive film stability of austenitic, ferritic, and martensitic SSs in deaerated sulphuric acid solution due to the presence of Cu in the passive film.

Therefore, in the section on ‘Mott–Schottky analysis’, effect of Cu on the defect density of the passive film will be investigated, which will enable us to understand the role of Cu in decreasing the passive film stability of SSs.

Mott–Schottky analysis
The defect density of the alloys was analyzed by Mott–Schottky analysis, which provides precise information on the electronic properties of the passive films. The analysis was carried out on the passive films formed at 0.4 and 0.8 V(SCE) respectively, for 9 h in pH 8.5 buffer solution at room temperature, as shown in Fig. 4a and b.

For the Mott–Schottky analysis, the specific interface capacitance (C), is obtained from
\[ \frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon_n N_D} \left( E - E_{FB} - \frac{kT}{e} \right) \] (1)
\[ \frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon_n N_A} \left( E - E_{FB} + \frac{kT}{e} \right) \] (2)

2 XPS depth profiles for passive films formed at 0.4 V(SCE) for 24 h in deaerated pH 8.5 borate buffer solution on a Fe–20Cr–0Cu alloys and b Fe–20Cr–4Cu alloys at room temperature

3 a relative concentration of Fe, Fe/(Fe+Cr) and Cr, Cr/(Fe+Cr) in Fe–20Cr alloy, b relative concentrations of Cr, Cr/(Cr+Fe), Cu/(Cr+Fe) and [%, Cu and Fe respectively in Fe–20Cr–4Cu SS alloy
where \( \varepsilon \) is the dielectric constant of the oxide (15.6 for Cr substituted \( \gamma \)-Fe\(_2\)O\(_3\)), \( \mu_0 \) is the vacuum permeability \( (8.854 \times 10^{-14} \text{ F cm}^{-1}) \), \( e \) is the charge of an electron, \( N_D \) and \( N_A \) are the donor and acceptor density in the passive film, respectively, \( E \) is the applied potential. \( E_{\text{app}} \) and \( E_{FB} \) is applied potential and flat band potential respectively, and \( k \) is the Boltzmann constant. Therefore, for \( n \)-type and \( p \)-type semiconductors, \( C_{2}^{2} \) versus \( E \) should be linear with positive and negative slopes that are inversely proportional to the \( N_D \) and \( N_A \) respectively.

The Mott–Schottky plots for the passive films formed on Fe–20Cr and Fe–20Cr–xCu alloys were taken at 0-4 V(SCE) (passive region) and 0-8 V(SCE) (transpassive region), as shown in Fig. 4a and b. Mott–Schottky plots for the passive films of Fe–20Cr and Fe–20Cr–xCu were very similar in shape, confirming that the passive films on these alloys are very similar and Cu addition did not change the base structure of the passive film in Cu containing alloys. Mott–Schottky plots at 0-4 V(SCE) (Fig. 4a) exhibited two linear regions. Positive slope in the potential region higher than –0-4 V(SCE) demonstrated \( n \)-type semiconductivity, related to (Fe, Cr) oxide for both of the alloys. On the other hand, the negative slope in the potential region lower than –0-4 V(SCE) showed \( p \)-type semiconductivity attributed to an inner Cr enriched oxide for both alloys.\(^{25,26}\)

The dominant and detectable donor species in \( n \)-type passive film were oxygen vacancy \( V_{O}^{2-} \) and the dominant acceptor species in \( p \)-type passive film were metal vacancy \( V_{V}^{3+} \).\(^{19,25}\) When the passive film was formed at 0-8 V(SCE) in Cr transpassive region, two linear regions with two positive slopes above –0-4 and 0 V(SCE) were observed respectively, as shown in Fig. 4b. The second linear region at potentials higher than 0 V(SCE) was attributed to the existence of \( V_{O}^{2-} \) ions acting as the deep donor in the passive film.\(^{25}\)

Table 1 showed the values of acceptor density \( (N_A, \ V_{O}^{2-}) \) and donor density \( (N_D, \ V_{V}^{3+}) \) calculated on the basis of equations (1) and (2) at 0-4 and 0-8 V(SCE) respectively.

The flat band potential \( (E_{FB}) \), represents a region where predominant electronic defects establish the transition between \( p \)-type and \( n \)-type semiconductivity. It determines the position of energy bands with respect to redox potentials of electro active ions in the electrolyte. The charge transfer in turn governs these positions across the semiconductor/electrolyte interface, the contact potential between semiconductor and electrolyte, interface, and the stability of the semiconductor. Flat band potential of the passive films formed at 0-4 and 0-8 V(SCE) was measured based on equation (1), for \( n \)-type passive film, where as equation (2) can be used to measure \( E_{FB} \) for \( p \)-type passive films. A tangent was drawn on X-axis from the linear region with positive slope \([-0-4 \text{ to } 0 \text{ V(SCE)}]\) and the corresponding value was taken as \( E_{FB} \) for \( n \)-type passive films and it was found to be nearly similar [from –0-39 to –0-42 V(SCE)] irrespective of the film formation potential. A positive slope higher than flat band potential indicated that the passive film behaved like \( n \)-type semiconductor (donor density/oxygen vacancy and metal interstitials), while at potentials lower than this, a straight line with a negative slope was observed suggesting that a \( p \)-type semiconducting behaviour (acceptor density). Consequently the passive film acts as a Schottky barrier above and below the flat band potential.

The donor density \( (N_D, \ V_{V}^{3+}) \) of the Cu containing alloys was higher than those without copper, as shown in Table 1, and this means that concentrations of \( V_{O}^{2-} \) of the passive films is increased by Cu addition. An increase in the acceptor density \( (N_A) \) of copper

![Mott–Schottky analysis of passive films](image)

**Table 1** Donor and acceptor density of Fe–20Cr and Fe–20Cr–xCu alloys at U\(_{f}\)=[0-4 & 0-8] V(SCE)], in deaerated pH 8-5 borate buffer solution at room temperatures, based on data of Fig. 4

<table>
<thead>
<tr>
<th>Samples</th>
<th>( U_{f}=0-4 \text{ V(SCE)} )</th>
<th>( U_{f}=0-8 \text{ V(SCE)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( N_D/\text{cm}^{-3} )</td>
<td>( N_A/\text{cm}^{-3} )</td>
</tr>
<tr>
<td>Fe20Cr</td>
<td>( 4.5 \times 10^{20} )</td>
<td>( 2.28 \times 10^{21} )</td>
</tr>
<tr>
<td>Fe20Cr4Cu</td>
<td>( 5.8 \times 10^{20} )</td>
<td>( 3.01 \times 10^{21} )</td>
</tr>
</tbody>
</table>
containing alloys was also observed, which means that Cr\(^{3+}\) concentration of the passive film was decreased (Fig. 5a). A similar trend was observed when the analysis was carried out at 0-8 V(SCE). There was no significant change in shallow donor density (\(N_{D1}\), \(V_{O}^{2+}\)), however deep donor density (\(Cr^{6+}\), \(N_{D2}\)) was increased to compensate the charge neutrality in the film as shown in Fig. 5b. Mott–Schottky analysis along with XPS data, suggest that copper is incorporated/dissolved in the Cr substituted \(\gamma\)-Fe\(_2\)O\(_3\) spinel structure as discussed in the previous section based on XPS results. The results can be further explained by charge neutrality principle, according to which, the substitution of Fe\(^{3+}\) by Cu\(^{2+}\) in the passive film decreased the positive charge of the passive film. This decrease in positive charge was compensated with the increase in concentration of \(V_{O}^{2+}\) and/or \(Cr^{6+}\) to satisfy the charge neutrality in the film.

A similar trend has been reported earlier while discussing the Mott–Schottky behaviour of Ni and Mo containing Fe–20Cr stainless steel alloys. An incorporation of Ni\(^{2+}\) into the Cr substituted \(\gamma\)-Fe\(_2\)O\(_3\) spinel structure by substituting Fe\(^{3+}\) would reduce positive charge in the film, thereby promoting the formation reaction of \(V_{O}^{2+}\) and/or the transpassive oxidation of Cr\(^{3+}\) to \(Cr^{6+}\) to supplement the positive charge in the passive film. In contrast, Mo\(^{4+}\) and Mo\(^{6+}\) dissolved in the Cr substituted \(\gamma\)-Fe\(_2\)O\(_3\) by substituting Fe\(^{3+}\) cause excessive positive charge, which should reduce the concentration of \(V_{O}^{2+}\) and/or \(Cr^{6+}\) to satisfy the charge neutrality in the film. The results lead to the decrease in the shallow donor density and/or deep donor density respectively in the passive film.

Therefore, it is concluded that some copper is enriched/incorporated/dissolved in \(\gamma\)-Fe\(_2\)O\(_3\) in Fe–20Cr–xCu alloys by substituting Fe\(^{3+}\) and passive film on these alloys becomes (Cu + Cr) substituted \(\gamma\)-Fe\(_2\)O\(_3\). Therefore, the Cu addition increased the shallow donor density and/or deep donor density of the passive film. The decrease in Cr\(^{3+}\), concentration of the passive film, was confirmed by the higher acceptor density (\(N_{A}, V_{Cr}^{-}\)) of p-type passive films formed on Fe–20Cr–xCu alloys than those on Fe–20Cr–0Cu alloys.

Therefore, the passive film formed on Cu containing alloys is less stable and protective in nature as compared to Cu free alloys. Having such a passive film will decrease the localized corrosion resistance, repassivation rate and stress corrosion cracking resistance of the stainless steel alloys as reported previously by Toor et al. They have investigated the effect of Cu on the repassivation kinetics and found a significant decrease in repassivation rate of films in Cu containing alloys.

**Discussion**

Point defect model of Macdonald et al. states that the minor alloying elements can form a solid solution with major alloying elements, when a passive film is formed. Therefore, these minor alloying elements, in other words, can modify the passive film properties by dissolving in the film (as dopants) and will affect the defect chemistry of the passive film. The physico-chemical properties of the passive film could be dominated by the point defects such as oxygen vacancies, metal interstitials and metal vacancies, with high concentrations (usually \(10^{19}-10^{21} \text{ cm}^{-3}\)), which are responsible for mass transport for the oxide growth. In terms of defect density of the passive film, the solubility of Cu in the passive film in Fe–20Cr–xCu alloys, either substitutional or interstitial, will increase or reduce the point defect concentrations. Subsequently, the variation will improve or weaken the corrosion resistance through the respective inhibition or enhancement of the mass transport. The suppression of defects or imperfection will favour the formation of a more compact layer with a lower porosity, but the promotion leads to formation of a more porous, open and consequently thicker layer. As in this study, it was found that the Cu enrichment in the passive film, increased the defect density of the film, so it can be stated that Cu has decreased the passive film stability and protectiveness.

It is well known that \(\gamma\)-Fe\(_2\)O\(_3\) has a spinel structure containing vacancies and ferric ions in its tetrahedral or octahedral sites. Orgel et al. reported that Fe\(^{3+}\) ion in spinel structure resides at the same energy level irrespective of whether it is as octahedral sites or at tetrahedral sites, but Fe\(^{3+}\) ions are more stable at octahedral sites than at tetrahedral ones. Belo et al.
reported the effect of Cr and Cu on the semiconducting properties and discussed in detail the basic aspects of crystallographic spinels which are important in describing the electronic structure of passive films formed on iron based alloys. They have stated that the way different ionic species distribute in tetrahedral and octahedral sites contained in an oxide lattice, determines the defects, i.e. donor or acceptor, energy levels in the band gap of the that particular oxide. It was also reported that chromium cation can be incorporated in the octahedral positions of the spinel and this phenomenon will lead to the formation of a larger range of spinels with chemical composition situated between that of the magnetite inverse spinel and that of the direct spinel (chromite). As mentioned earlier, this study has found based on Mott–Schottky analysis and XPS investigations, that Cu was incorporated in the passive film. This copper has occupied some of the tetrahedral and octahedral sites substitutionally, previously being occupied by Fe\(^{3+}\) and Fe\(^{2+}\) sites respectively. Atrens et al.\(^{32,33}\) have discussed in detail the role of Mo and oxygen with various chemical binding states, on the passivity and its breakdown in stainless steels. It was found that oxidised Cr and Fe form the main components within the passive film on stainless steels and there is generally more Cr oxide in the outermost layer of the passive film in comparison with oxides of iron and other alloying elements, which imparts these alloys excellent corrosion resistance properties due to formation of protective passive film. Since the defect density or electronic properties are ultimately related with the corrosion resistance of stainless steels, so an increase in defect density can significantly decrease the corrosion resistance ability of a particular alloy, i.e. Fe–20Cr–xCu. So it can be concluded based on these investigations that Cu incorporation/enrichment in the passive film increased the defect density of the passive film, which ultimately decreased the passive film stability and corrosion resistance properties of Cu containing stainless steel alloys.

Conclusions

Potentiodynamic polarisation tests, Mott–Schottky analysis as well as XPS investigations of the passive films on Cu containing stainless steels revealed the following conclusions.

1. Cu addition increased the anodic dissolution or the oxidation of iron to iron oxide as well as the passive current density, in deaerated pH 8-5 borate buffer solutions.
2. XPS analysis found copper enrichment in the passive film of Fe–20Cr–xCu alloys. Copper was mainly present in the outer few nanometres and decreased as the depth of film was increased.
3. Mott–Schottky analysis showed that, passive film on Cu containing alloys was (Cu+Cr) substituted \(\gamma\)-Fe\(_{2}\)O\(_{3}\). Also the addition of copper increased the acceptor density (decreased the Cr\(^{3+}\) concentration) of the passive film at 0-4 and 0-8 V (SCE) respectively, which resulted in less protective and stable passive films on copper containing alloys. Results also showed that both the shallow donor and deep donor densities were increased due to Cu addition in Fe–20Cr–xCu alloys. These results lead to the conclusion that Cu presence in Fe–20Cr–xCu alloys will decrease their localised corrosion resistance properties, due to formation of a less stable and protective passive film on their surface.

Acknowledgement

The authors gratefully acknowledge the support provided by King Fahd University of Petroleum & Minerals (KFUPM) Saudi Arabia, under the research grant #1N121033 for conducting this research.

References