PREDICTING THE CORROSION AND STRESS CORROSION
PERFORMANCE OF COPPER IN ANAEROBIC SULFIDE SOLUTION

BY

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ABSTRACT

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Stress corrosion cracking (SCC) susceptibility of the phosphorus de-oxidized copper has been evaluated in synthetic seawater polluted by sulfides using slow strain rate test (SSRT). The effect of concentration of sulfide, temperature, and applied cathodic and anodic potentials on the final strain values and maximum stress were also studied. No cracks were found under the tested conditions. The final strain and maximum stress values decreased but not significantly, with increase in the temperature, applied anodic potential and sulfide concentration. The observed effect is due to the section reduction by uniform corrosion. Lateral cross section and microscopic examination of the fractured specimen ruled out the existence of the localized corrosion. Electrochemical measurements showed that the Cu₂S film is not a protective film and also exhibits a mass transfer limitation to the inward diffusion of the sulfides. Based on these results the reasons for the absence of cracking are also discussed.
To my mom Uma, my dad Bhaskaran
for their unconditional love, support and understanding
throughout my life.
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1.1 Introduction

Based on the level of radioactivity, nuclear wastes are classified into three categories: a) High level waste (HLW) b) Intermediate level waste c) Low level waste. Spent fuel and waste from fuel reprocessing plants are the principle sources of HLW. This type of waste requires adequate cooling as it generates considerable amount of heat, radiation shield is also required as waste contains highly radioactive fission products and long-lived radioactive elements. The reprocessed waste is either vitrified by incorporating in glass (e.g. borosilicate, phosphate) or sealed in concrete containers. The vitrified waste is then placed in a metallic canister [1].

1.2 Disposal of HLW

For the long-term disposal of HLW, the metallic waste canister is buried deep underground in a geological repository. To prevent the contact of the radioactive waste with the environment, in an event of canister failure, a three-stage barrier protection is in place.

1. First barrier is the inherent stability of the solidified waste and as well as the metallic canister against the attack of water and/or other corrosive elements.
2. The second is the role of the geological containment itself. This prevents the contact between contaminated water within the containment and the circulating groundwater.

3. Finally, presence of large amount of soil and rocks between the surface and the repository provides a huge sorption capacity thereby retarding spread of the radioactive elements.

1.3 Current Scenario

In countries like Canada and Sweden, copper has been identified as the suitable material for the storing nuclear waste. The current design consists of a pressure barring cast iron as the inner cylinder and corrosion resistant copper as the outer layer. The canister is designed to withstand a stress of 45 MPa; this is equivalent to the hydrostatic pressure exerted in the event of glacier formation above the repository. The space between the granite rock and the waste canister is filled with bentonite clay. Phosphorus de-oxidized high pure copper has been chosen for this application, the concentration of oxygen is less than 5 ppm. The addition of 45 ppm of phosphorus improves the creep resistance of the metal considerably. The dimensions of the canister and the fuel assembly slots are designed in such way that the temperature on the surface of the copper should not exceed 100°C [2].

Copper is immune to corrosion under anaerobic conditions. Generally, the ground water in granite vault contains virtually zero concentration of oxygen due to the existence of the anaerobic conditions; however oxygen is incorporated during the mining and placement of the waste canister. According to the literature data, the initial aerobic period will last about 10-300 years after the closure of the repository; the bacteria in the shafts and tunnels of the repository would effectively
consume the oxygen. The minerals in the granite shield will also consume oxygen to some extent [3]. However in the presence of the sulfides, the stability of the copper is greatly affected. The principle reason behind this behavior is due to the formation and stability of the copper sulfides as it’s indicated in the Pourbaix diagram Figure 1 [17].

Figure 1: Pourbaix diagram of copper in water containing sulfides [HS\(_{-}\)]\(_{TOT}\) = 0.2 mmol/kg and [Cu\(_{TOT}\) = 10\(^{-6}\) mol/kg at 25°C.

The following are sources of the tensile stress factors
- Residual stress that arise during the canister manufacture and closure welding procedures.

- Hydrostatic pressure of 45 MPa, in the event of glacier formation.

- Finally, the load of about 8 MPa exerted by the swelling of the bentonite clay.

1.4 Thesis Objectives

Calculations based on the present sulfide concentrations would not affect the integrity of the copper over 100,000 years. However, due to the co-existence of the stress factors mentioned above and the corrosive environment may trigger a stress corrosion cracking (SCC).

1. The primary objective of this research work is to evaluate the susceptibility of the phosphorus de-oxidized high pure copper to SCC in the presence of the sulfides under anaerobic conditions.

2. To study the effect of the factors like temperature, sulfide concentrations and the applied electrochemical potential on the SCC performance of high pure copper in sulfide polluted synthetic seawater.

The second chapter deals with relevant literature review on the sulfide corrosion and SCC of both copper and its alloys. The third chapter describes about the experimental procedures that were followed for this research work. The fourth chapter contains in-depth analysis of the key results and the final chapter summaries the conclusion and the recommendations that were drawn out of this research work.
2.1 Stress Corrosion Cracking (SCC)

SCC is the gradual growth of cracks under the simultaneous influence of a nominal static and or tensile stress and a chemical reactive environment. For metals, reactive environment does not include gaseous $\text{H}_2$, cathodic polarization and liquid metals [4]. SCC is always accompanied by microscopic plastic strain and many believe that such strains occurring dynamically at crack tip are a causal factor of crack growth. Several factors like metallurgy of the metal, environment influence the crack initiation and propagation in SCC.

2.2 Role of Environment

The region II of the Figure 2.1 indicates that apart from the mechanics of the process, there exist some other factors, which control the crack propagation. This means some chemical component is influencing crack growth. The following are the chemical factors, which could influence the crack velocity [5]

1. Rate of oxidation or dissolution at the crack tip. The environment in the crack, including the local potential controls this factor.

2. Adsorption/diffusion rate of $\text{H}_2$.

3. Rate of surface diffusion process of metal atoms or ions.
2.3 Role of Electrochemistry

Although electrochemistry comes under environment factor category, based on the current literature reports, there are about six different electrochemical circumstances where SCC occurs. They are

- An actively corroding state where SCC is predominantly due to the hydrogen absorption e.g.: cracking of high strength steel in salt water.
- A borderline passive state, where SCC is due to the anodic process at the crack tip e.g.: carbon steel cracking in hot caustic or nitrate environment.
• A slow rate of localized corrosion in a halide solution e.g.: austenitic stainless steel in hot chloride. If the corrosion process is faster it results in blunting of the crack tip.

• Presence of dealloyed layer triggering a brittle crack through unattacked substrate e.g.: dezincification of brass in ammonia solution.

• A state of mild transpassivity as it is seen in the case of Cr (VI) dissolution in stainless steel.

• A stable filmed state, but the film growth kinetics, especially at deformation features are such as to allow a certain rate of cracking despite little or no dissolution e.g.: cold worked austenitic stainless steel in hot water.

Apart from these criteria there are few SCC cases which cannot be classified under either defective metallurgy or environment category e.g.: transgranular cracking of carbon steel in anhydrous liquid ammonia, intergranular cracking of nickel alloy 600 in reducing hot water. In short, most of SCC cases can be summarized as: SCC may occur if proper metallurgy conditions and stress exists, most importantly when the metal is passive but not too passive. Similarly most SCC cases require an interaction between the environment, the bare metal and the passive film. The mechanism behind the crack growth due to the anodic dissolution or hydrogen embrittlement is not always clear. The idea of SCC spectrum proposed by Parkins [6] is still valid today. In this spectrum SCC due to anodic dissolution and hydrogen effects occupies the extreme ends of the spectrum.
2.4 SCC Models

Several authors have proposed universal models of SCC or even for environment-assisted fracture in large. However these models are only valid to particular systems, they are not universal. Most of SCC cases in metals come under any one of the following three models.

Figure 3: 1980 SCC spectrum by Parkins

(i) *Slip dissolution model:*

This model was initially favored for both intergranular and transgranular cracking, but now it’s mainly applied only for intergranular cracking. According to this model, crack initiation occurs by extremely localized anodic dissolution. Crack propagation was by a cyclic process of film rupture, metal dissolution and followed by film repair. The walls of the cracks are covered by the protective oxide film, which is fractured due to the plastic strain in the metal at the crack tip e.g: intergranular cracking of ferritic steel in passivating environment such as carbonate or bicarbonate.

(ii) *Film induced cleavage model:*

Edeleanu and Forty proposed this model for the superficial dezincification of alpha brass in ammonia solution. They observed that the measured high crack velocity values could not be accounted by possible anodic dissolution rates. Later it was proposed that the superficial thin nano porous dealloyed layer that is formed during the corrosion of alloy containing high amount
of less noble metals triggered a brittle fracture through several micrometers of the unattacked substrate. Initially it was conceived that the property of the FCC metal substrate was responsible for the high crack velocity, however modern film induced cleavage models credit this special property to that of the nano porous layer. The layers are produced by dealloying are both brittle and epitaxial in nature, so they are strongly bonded to the substrate. Intergranular fracture in Ag-20 at% Au alloys in perchloric acid is explained by this theory.

![Figure 4: Schematic representation of slip dissolution model (left) and film induced cleavage on (right).](image)

(iii) **Hydrogen Embrittlement:**

When atomic hydrogen is absorbed into an alloy, the toughness and the ductility can be reduced significantly and even subcritical crack growth can occur. SCC of high strength steels in aqueous solutions is a very good example of this phenomenon. Similarly sulfur adsorption in H₂S environment on the steel poisons the hydrogen recombination reaction \( \text{H} + \text{H} \rightarrow \text{H}_2 \) leading to the absorption of 100% of the discharged hydrogen into the metal. Due to the small size of the
hydrogen atom, it can easily diffuse into some metals even at room temperature. The acidification of the local environment due to the cation hydrolysis leads to the concentration of the hydrogen at the fracture zone, ahead of the crack tip. The presence of the tensile stress near the crack tip results in the expansion of crystal lattice. This in turn increases the solubility of hydrogen locally. The atomic hydrogen reduces the bond strength between the metal atoms, leading to the cleavage, intergranular separation or a highly localized plastic fracture. The embrittlement effect decreases at high temperatures, as the atomic hydrogen escapes from the metal lattice as gaseous hydrogen [7].

2.5 Copper in Alkaline Medium

Corrosion of copper is supported by oxygen reduction; the pH has a greater control over the corrosion rate, mainly due to the oxide film formation. Above pH 4, the formation of cubic Cu$_2$O is favored and further increase in pH results in formation of smaller Cu$_2$O crystals resulting in thinner and compact oxide film [8]. The oxide layer is a semiconducting film exhibiting both p and n type conductivity depending on the conditions; depending on pH soluble species of Cu$^+$ and Cu$^{2+}$ are detected during the oxide formation [9].

2.6 Sulfide Corrosion of Pure Copper

This oxide formation is significantly retarded when small amount of sulfide is added to this environment. Corrosion of copper in the presence of sulfide ions is a spontaneous process in oxygen free solutions. Even though this corrosion process has been studied for decades, the mechanism of the formation of copper sulfide is still under debate. King and Stroes-Gascoyne [10] observed that the corrosion potential ($E_{corr}$) dropped to an active value, when the
environment was evolving from aerobic to anaerobic, during the corrosion of copper in chloride solution. This shift was much more dramatic when small concentration of sulfide was added. Depending on the sulfide concentration, the final rest potential value ranged from -0.8 to -1 V vs. saturated calomel electrode (SCE). They measured $E_{corr}$ values of -0.9 V vs. SCE in 0.3 mM HS$^-$ solution and -0.96 V vs. SCE in 3.3 mM HS$^-$ solution. This value was very close to the one measured by Escobar et al. [11], who studied the sulfide corrosion in the temperature range of 15°C to 90°C. From the Tafel curves, they calculated the $E_{corr}$ values -0.96 and -1.08 V vs. SCE for the sulfide concentrations of 1 and 100 mM/dm$^3$ respectively in water. The calculated corrosion rates ranged from 10 to 100 µm/year and the highest corrosion rate was for 100 mM and 90°C. The reported values were for the scenario in which there were no transport limitations of the sulfide ions to the copper surface. Such scenario would only exist if a sulphate reducing bacterial bio film covers the whole surface of the copper; this is highly unlikely because of the low availability of water [12].

Hermansson and Eriksson [13] conducted a long-term (>6 months) immersion experiment of copper in deaerated synthetic groundwater containing 41 ppm of sulfides as Na$_2$S at 20°C. They observed that the surface film formation was faster in presence of sulfides and after the long time exposure, the corrosion products contained very little amount of sulfur; while copper and oxygen were the dominant elements.

Taniguchi and Kawasaki [14] also carried out a long time (736 days) immersion studies as part of their investigation of corrosion behavior of pure copper in sulfide polluted synthetic seawater. The reported corrosion rates were 3.8 µm/year and 9.7 µm/year for 5 mM and 10 mM Na$_2$S concentration respectively in case of simple solution at 80°C. These values were less than the
ones reported by Escobar et al. [7]. The reason for the low values could be due to the depletion of the sulfide ions during the course of the experiment. For bentonite-sand mixture medium the reported corrosion rates were similar to simple solution case; however the morphology of the corrosion products were different. They observed a patchy corrosion product layer in case of bentonite-sand mixture and for the simple solution the corrosion product was very adherent to the copper surface. The XRD measurements showed that the corrosion layer predominantly contained chalcocite (Cu₂S) for high sulfide concentration (≥ 5 mM Na₂S concentration). The copper substrate was corroded uniformly in both the solutions and there was no sign of localized attack.

J. Smith et al. [15] studied the conversion of preformed Cu₂O to Cu₂S. For the lower sulfide concentration (2 x 10⁻⁷ mol/L) the conversion rate was less that suggested a threshold would exist at even lower concentration. The conversion process is purely chemical in nature and complete conversion was indicated by the transition in E_{corr} value close to E_{c}(Cu/Cu₂S). The sulfidation process occurs in three stages leading to complete conversion with 100% efficiency. At initial stages, the morphology of the transition film is similar to that of the pre-grown oxide film, but in the final stage it forms a highly porous sulfide film. The time dependence of the complete conversion (Cu₂O to Cu₂S) indicated a reaction order of 0.8 that suggested the process was close to a first order reaction.

Hilden et al. [16] studied the effect of anions like Cl⁻ and HS⁻ on the oxide film of copper exposed to water at pH 8.9 (0.1 M borax as buffer) at 80°C and 2 MPa pressure. Chloride caused a breakdown in surface film under oxidizing conditions i.e. in the stability region of divalent copper. However on the reducing environment, chloride did not have any effect on the stability of the film.
In presence of 10 ppm of H₂S, the calculated average surface film thickness was 10 times thicker and defective than the film formed in a pure borax solution.

Escobar et al. [17] conducted a XPS analysis on the surface films of copper, when exposed to the 1 and 100 ppm sulfide solutions under aerobic conditions. Adherent sulfide film was only observed at highest sulfide concentration (100 ppm). The lack of formation of such film at low sulfide concentrations was ascribed to the presence of residual oxygen in the ground water. This paper clearly shows that presence of dissolved oxygen in water is detrimental to the stability of sulfides.

Similar observations were made by Abd El Haleem [18] in aerated alkaline solution. At low sulfide concentration (≤ 10⁻⁴ mol/L), Cu₂O formation was favored. At intermediate concentration (10⁻³ mol/L), there’s a fluctuation between active and passive region. At high concentration (10⁻² mol/L), only Cu₂S was favored.

### 2.7 Sulfide Corrosion of Cu alloys

More than the sulfide corrosion of pure copper, much work has been carried out on Cu-Ni alloys. These alloys are specifically used in marine environment because of their excellent resistance to corrosion in seawater. The incorporation of Ni and Fe atoms in the copper compound lattice decreases the defect number; as a result passivating power of the corrosion layer significantly increases. In presence of sulfide, the protective oxide film is replaced by a non-stoichiometric sulfide film, which in turn severely brings down its corrosion resistance.
Bode and Popplewell [19] studied the corrosion of 90Cu-10Ni alloy in sulfide polluted aerated and deaerated seawater. They observed that the corrosion rate was low in deaerated sulfide polluted seawater and the rate was high when the sample was transferred to aerated unpolluted seawater. A 2-day sulfide exposure resulted in accelerated corrosion attack for 5 days in unpolluted system before the corrosion rate returned to a minimal value. They proposed that the exposure to sulfide resulted in prevention of the formation of the protective copper oxide film on the surface. Inclusion of Cu$_2$S into Cu$_2$O resulted in the increased electronic and ionic conductivity within the film. The crystal mismatch yielded a highly porous interface for solution based mass transport to the alloy surface to sustain corrosion. These reasons resulted in an accelerated attack after transferring it to aerated unpolluted seawater.

C. Kato and H. W. Pickering [20] studied the effect of 5 ppm of sulfide in de-aerated seawater on the corrosion mechanism of Cu-9.4Ni-1.7Fe at room temperature. The thickness of the surface film in sulfide polluted sea water was greater than the one in sulfide free solution. After the immersion for certain days, the corroded samples were placed in sulfide free deaerated and aerated 3.5% NaCl for anodic and cathodic polarization measurements respectively. Though there was no appreciable change in anodic polarization curves, the cathodic polarization curves of sulfide containing surface films were polarized very much less compared to the surface without sulfide films. The increase in corrosion current was attributed to the increased oxygen reduction rate due to the catalytic nature of the porous sulfide film. When this porous sulfide layer was stripped leaving behind the thin adherent layer, the measured corrosion current subsequently decreased.
J.N. Alhaji and M. Reda [21] evaluated the corrosion resistance of 90Cu-10Ni and 70Cu-30Ni in seawater polluted by 10 ppm of sulfide. In the presence of sulfide the corrosion reaction was under the anodic control, while for other pollutants like urea, ammonium chloride it was under cathodic control. βa values of 90Cu-10Ni and 70Cu-30Ni increased from 45 to 500 mV/decade and 70 to 200 mV/decade respectively in presence of 10 ppm of sulfide. This was attributed to the formation of non adherent, brittle, non protective sulfide layer under stagnant conditions affect the anodic reaction by strengthening the effects of concentration polarization. However, the corrosion rate values determined by linear polarization increased up to one order and threefold magnitude for 90Cu-10Ni and 70Cu-30Ni respectively. They concluded that in the presence of sulfide the corrosion reaction was under cathodic control and in absence of sulfide, it corrosion was under diffusion control due to the presence of trace oxygen. They also proposed a corrosion mechanism.

Cathodic reaction in deaerated seawater:

$$2H_2O + 2 e^- \rightarrow 2 OH^- + H_2$$

Anodic reaction:

$$Cu/Ni + HS^- \rightarrow Cu/Ni (HS^-)_{ads}$$

$$Cu (HS^-)_{ads} \rightarrow Cu (HS) + e^-$$

$$Ni (HS^-)_{ads} \rightarrow Ni (HS)^+ + 2e^-$$
\[
\text{Ni} \,(\text{HS})^+ \rightarrow \text{Ni}^{2+} + \text{HS}^-
\]

\[
2\text{Cu}^+ + \text{HS}^- + \text{OH}^- \rightarrow \text{Cu}_2\text{S} \downarrow + \text{H}_2\text{O}
\]

\[
\text{Ni}^{2+} + \text{HS}^- + \text{OH}^- \rightarrow \text{NiS} \downarrow + \text{H}_2\text{O}
\]

The Cu$_2$S film act as an effective cathode for water reduction in deaerated solution.

Macdonald et al. [22] studied the corrosion of Cu-Ni alloys in deaerated sulfide polluted seawater. The polarization resistance (R$_p$) drastically reduced when small concentration of sulfide ($\leq 0.85$ mg/L) was added. For higher sulfide concentration ($> 0.85$ mg/L), the decrease in polarization resistance values was not that significant. The drop in R$_p$ values was ascribed to the formation of non-protective sulfide film over the passive oxide film. The electrochemical impedance measurement indicated that the charge transfer resistance also drastically reduced with the addition of sulfide. XRD measurements on the corrosion products revealed the presence of Cu$_2$S and non-stochiometric sulfides of copper (Cu$_{1.8}$S). It was concluded that, the corrosion of Cu-Ni alloys in anoxic sulfide solution identical to pure copper sulfide corrosion.

### 2.8 Electrochemical Investigation on copper sulfides

D. Vasquez et al. [23] reported that there were three distinct regions in the anodic polarization curve of sulfide film formation of copper. The first region corresponded to nucleation and growth of a complex sulfide layer at a potential close to Cu/Cu$_2$S and Cu/CuS reversible electrode potential. The second region was attributed to the rupture of the Cu$_2$S layer leading to the formation of poorly protective CuS layer and this led to the pitting of the base metal. The
final region was for the electro oxidation of the base metal but the formation of the copper oxide was delayed due to presence of the sulfide layer resulting in dissolution of copper. The film growth mechanism of nucleation and growth fitted perfectly with experimental data. A hemispherical diffusion zone was established around each growing nucleus. These diffusion zones overlap with each other resulting in the formation of linear diffusion zone towards effective planar surface. During the oxidation process, no soluble copper ion species were found. The sulfidation of copper in aqueous solution was similar to chemical sulfidation of copper. In the latter process, the sulfidation rate was controlled by the diffusion of copper through the sulfide layer of regular structure [24].

M.R. Gennero de Chialvo et al. [25] also observed similar trend while studying the electrochemical behavior of copper in alkaline solutions containing sodium sulfide. The electrochemical and optical data showed that the oxide formation was preceded by the sulfidation. The presence of sulfide delayed the oxide formation and accelerated the dissolution of copper. The sulfide also modified the cathodic potentiodynamic behavior of the complex copper oxide layer. This was due to the precipitation, of the soluble copper species that were formed during the oxide formation, by the sulfides. The kinetics of the sulfidation can be interpreted in two successive stages. The first stage was the formation of the monolayer, depending upon the pH at the interface i, one of the following two reactions would occur.

$$\text{Cu} + (\text{HS}^-)_i \rightarrow \text{Cu(}\text{HS})_{\text{adsorbed}} + e$$

The next stage corresponds to the oxidation of the copper to cupric sulfide.
Cu (HS) → CuS + H^+ + e

These reactions became mass transport controlled by the sulfide ion coming from the bulk solution to the electrode surface. Localized corrosion (pitting) occurs at more anodic potentials (> -0.150 V vs. SCE). The sulfur-containing species adsorbed at surface defects above a critical coverage value, thus preventing the passivation by copper oxides. This results in the weakening of metal-metal bond thus promoting the localized corrosion. In those places, where the coverage value is less than the critical coverage, copper oxide formation occurs.

Scharifker et al. [26] also confirmed the film growth mechanism of nucleation and growth. They restricted the Cu_xS film formation by limiting the anodic potential to values more negative than -0.5 V vs. SCE during the cyclic voltammetry scan in sulfide containing NaHCO_3. In this region, the ratio of the cathodic to anodic charge was found to be near 1, independent of pH, sulfide concentration and scan rate. This showed that there was no appreciable dissolution of copper or of the sulfide film in the potential range of -1.2 to -0.5 V vs. SCE. The XRD analysis confirmed the presence of single phase Cu_2S. The potentiostatic I-t behavior was consistent with a short time double layer charging followed by a current increase to a maximum value and subsequent decay to a constant value. This was a typical characteristic feature of film nucleation and growth process. Galvanostatic pulsing confirmed this feature too.

Kharafi et al. [27] reported an intergranular corrosion of copper in sulfide polluted salt water. They observed sulfide induced intergranular corrosion both at free corrosion potential and at more anodic potentials. A transition potential E_t (-0.195 V vs. SCE in 10^{-3} mol/L sulfide) promoted accelerated intergranular corrosion in sulfide polluted salt water. Below E_t, mainly copper
dissolution was promoted and above $E_t$, sulfide was oxidized to sulfate and sulfur. X-ray photoelectron spectroscopy (XPS) on the exposed surface under free corrosion potential showed only one peak at S2p 162.0 eV corresponding to Cu$_2$S. However XPS measurements at $E_t$ had additional peaks at 163.8 and 168.6 eV, these signals are associated with elemental sulfur and sulfate respectively. They also proposed that the reason behind the intergranular attack could be poor formation or protection of protective Cu$_2$O along grain boundaries due to the presence of impurities like Ni, Ag, Bi, Ta, As, P, et.c.

Rahmouni et al. [28] studied the corrosion of copper in sulfide polluted saltwater using electrochemical techniques like potentiodynamic polarization, impedance spectroscopy and electrochemical quartz crystal microbalance measurements (EQCM). The polarization measurements showed that the corrosion current decreased with increase in the sulfide concentration in the solution. For a 10 ppm sulfide concentration, the measured corrosion current was 5.20 $\mu$A/cm$^2$ whereas for the 0 ppm concentration the corrosion current was 15 $\mu$A/cm$^2$. Interestingly, the EQCM results were totally opposite, in the absence of sulfide the reported corrosion current was 0.91 $\mu$A/cm$^2$ and for the 10 ppm sulfide concentration it was 5.33 $\mu$A/cm$^2$. The impedance measurements were in an agreement with the EQCM results. The impedance data was fitted with an equivalent circuit containing two capacitive loops representing a porous film. The charge transfer resistance decreased and the double layer capacitance increased with increase in sulfide concentration, indicated the fact that the corrosion rate increases with increase in sulfide concentration. Galvanostatic experiments suggested that the corrosion of the copper was accelerated by the participation of OH$^-$ and HS$^-$ ions in parallel.
Srivatavasa et al. [29] studied the surface films on copper that was formed in sulfide, chloride, and ammonium ions polluted solutions using electrochemical impedance spectroscopy. After two hour immersion in 3.5 wt% NaCl + 100 ppm Na₂S + water the measured polarization resistance value was 7056 ohm cm² while after 432 h immersion, the value was 6220 ohm cm². Similarly for two hour immersion in 5 wt% NaCl + 100 ppm Na₂S + water the resistance value was 6417 ohm cm² and at the end of 432 h immersion, it was 2416 ohm cm². To fit the impedance data, two types of circuits were used. For the shorter immersion time, it was fitted with circuit equivalent to the porous film. The capacitors were represented by a constant phase element. For longer immersion time, the same circuit with an additional Warburg component was used. The porous film resistance values changed dramatically during the immersion time for both the solutions, however towards the end, they reached constant similar values. There were no dramatic changes in the charge transfer resistance values. Damage function analysis was also carried out on the calculated impedance values. According to the analysis, the surface became less protective on exposure to the solution containing chlorides, whereas the corrosion tendency decreased on exposure to sulfide ions. The presence of chlorides resulted in breakage of oxide layer leading to a relatively rough and deeply corroded surface. The linear polarization resistance decreased in solution containing only sulfide ions. Interestingly, the authors did not take into the account of the fact that the all sulfides would have got consumed during the 432 h exposure time. The measured open circuit potentials also corroborate this statement, as the potential values shifted to more noble values after 50 h immersion.

J. Smith [30] got two types of impedance data of copper in solution containing 10⁻³ mol/L sulfide under identical conditions. The first type of data was fitted with an equivalent circuit comprising
of a simple resistor, capacitor and a Warburg component. The single resistor represented the resistance of the surface film and the double layer similarly the capacitor represented the film and the double layer capacitance. The main difference between the two sets of the data was the behavior at the lower frequency region. The second type data had an additional time constant at the lower frequency, so a more complex circuit representing a porous film was used. The double layer capacitance decreased continuously during the exposure time, while the film capacitance decreased initially, but later reached a constant value. Both the pore and the double layer resistances increased with time, this indicated that the corrosion process yielded a resistive film on the surface. The increase in pore resistance was associated with the blockage of the pores by the sulfide film. The values of the capacitances and resistances were high in second type compared the first set. The reason for this behavior was the nature of the surface film. The first type of impedance data was associated to a compact sulfide film, leading to an inward sulfide diffusion limitation, while the second type was for the defective film, which resulted in the more transport of sulfide through the defects. The continuous corrosion process in the latter case yielded a much more resistance film than in the first case. However, under identical conditions the reason behind the formation of a compact or a defective film is still unknown.

2.9 SCC of Pure Copper

SCC of pure copper has been observed mainly in (a) ammonia, (b) acetate (OAc\(^-\)), and (c) nitrite (NO\(_2\)) environments.
(a) Ammonia:

Aqueous ammonia is the principal environment associated with the cracking of copper and its alloys in practical applications. Pugh and Westwood (25) showed that SCC of brass would not occur in the absence of dissolved copper. As the dissolved copper concentration in aqueous ammonia was increased, the time failure, decreased drastically. Beyond certain critical concentration of the copper, a tarnish film was formed on the surface. This film though reduced the corrosion rate, the severity of cracking continued to increase with increasing copper concentration in the tarnishing range. It was later shown that by polarizing the brass anodically, cracking was observed in copper-free ammonia solution. Thus it was inferred that the primary role of the dissolved copper or cupric complex ion as an oxidant in solution providing a cathodic reaction. Various mechanisms have been proposed for cracking of copper in ammonia environment. Film rupture/anodic dissolution have been proposed for both tarnishing and non-tarnishing environments. In both the cases, Cu₂O was formed at the crack tip. In case of a pure copper Thompson and Tracy [32] reported an intergranular stress corrosion cracking, followed by the rupture of protective Cu₂O film in aqueous ammonia. The cracking susceptibility increased with increase in the phosphorus content, as well as other alloying elements Zn, As, Sb, Ni, Al. Sieradzki and Kim [33] explained the cracking of oriented single crystal of pure copper through film induced cleavage in non tarnishing ammonia environment. The occurrence of cracking was correlated to the formation of a uniform microscopic porous layer, which was developed due to the effect of dynamic strain on etch pitting process. The cracking occurs only if a certain balance between the corrosion (etch pitting) and the strain rate was established. At too
high strain rate, failure was by normal ductile process, similarly too low strain rate, prevented the formation of sub micron size porous layer from etch pits.

(b) Acetate:

Escalante and Kruger [34] first reported the cracking of copper in sodium acetate solution. They observed an intergranular cracking in solution containing 0.025 M cupric acetate; however no cracking was observed in cupric sulfate solutions. A tarnish film was observed in both cases, with growth rates similar to that for brasses susceptible to SCC. Interestingly, light retarded the film formation on copper and prevented cracking in cupric acetate solution. In absence of the stress, oxide formed all over the surface, while in the presence of the stress, the oxide formation was concentrated in the grain boundaries. In the end, tarnish rupture model was attributed to the cracking mechanism.

Cassagne and Pugh [35] observed a transgranular cracking in 0.1 mol.dm\(^{-3}\) acetate solutions. The voltammetric and ellipsometric measurements indicated oxide film was formed in the pH range of 5.5 to 10.3 and no oxide was formed at and below pH 3. Voltammetry predicted that formation both of Cu\(_2\)O and CuO at high anodic potentials, but a constant refractive index from ellipsometry suggested that the presence of a single oxide. The oxide film breakdown occurs in acetate solution leading to the formation of a thick, poorly protective film. The slow strain rate test showed that the transgranular cracking was observed when there was an oxide film and normal ductile fracture was observed when there was no oxide formation. The applied potential also affected the mode of failure, the elongation to failure and the maximum engineering stress.
decreased with increase in the anodic potentials. It was also shown that the cracking could be suppressed by increasing strain rate. Even in the presence of an oxide film ductile fracture was observed at a strain rate of $8 \times 10^{-6}$ s$^{-1}$. This behavior was attributed to a competition between transgranular cracking and a ductile fracture. The film induced cleavage mechanism was ascribed for the cracking.

(c) Nitrite

Pednekar and Staehle [36] were the first group to report on the cracking of copper in nitrite solution. They observed transgranular cracking in 1 M NaNO$_2$ at pH 8.2. The fractured surface was covered with a brown-black oxide layer. Auger analysis of this film showed a 2.5:1 Cu/O ratio for a depth of 50 A°, no trace of nitrogen was detected in the film. The corrosion potential changed from 150 to 200 mV vs. standard hydrogen electrode (SHE), during the slow strain rate test. Since, this potential was higher than the equilibrium potentials of Cu/Cu$^+$ (165 mV vs. SHE) and Cu/Cu$^{++}$ (160 mV vs. SHE), it was suggested that the cracking was due to the anodic dissolution at slip steps. Sieradzki et al. [37] studied the effect of dynamic strain on the cracking of copper single crystals in nitrate solution. They reported a crack velocity value of 30 nm/s at 30°C. The fracture surface was cleavage-like, with striations parallel to crack front. When the dynamic straining was stopped, the cracks also stopped growing. This was behavior was attributed to the requirement of large displacement to form the steps between adjacent cleavage-like facets. The acoustic and electrochemical noise measurements suggest that the cracking proceeds by discontinuous cleavage. Benjamin et al. [38] and Yu et al. [39] found the minimum threshold concentration of NO$_2^-$ and the electrochemical potential below which the cracking was
not observed during slow strain rate test. For the phosphorus de-oxidized high pure copper, below the potential (-100 mV vs. SCE) and NO$_2^-$ concentration of 0.003 mol.dm$^{-3}$, cracking was not observed. Both reported a transgranular cracking with cleavage like fracture surfaces with crack arrest markings, similar to the findings of Sieradzki’s group. Additionally, Benjamin’s group reported that the cracking susceptibility decreased in case of both oxygen free high pure copper and phosphorus doped pure copper, with increase in temperature.

Beavers et al. [40] investigated the susceptibility of pure copper (CDA 102) and copper nickel alloy (CDA 715) in simulated well water of tuff repository. CDA 102 was susceptible to SCC even at 200 ppm of nitrite; however cracking was not observed in simulated well waters. It was assumed that the species in the simulated water inhibited SCC in dilute NaNO$_2$ solution. On the other hand anodic polarization of CDA 102 increased the susceptibility to transgranular cracking. Similarly, in slow strain rate test of CDA 102 at 90$^\circ$C cracking occurred under anodic polarization. Alloy CDA 715 was resistant to SCC in all environments. In some cases, the concentration of nitrite was increased to 1M, even then all the samples showed a negative result to cracking, except for one case, where possible incipient crack were observed in the necked region. However, the cracking could not be reproduced in subsequent test. The mechanical properties like ultimate tensile strength, reduction in area did not significantly change with the nitrite concentrations.

Rosborg and Werme [41] reported both transgranular and intergranular cracking in 0.3M NaNO$_2$ solution. There was a strong potential dependence on the cracking was observed. SCC was observed at corrosion potential in deaerated solution, but no cracks were observed when the
The sample was polarized to -150 mV vs. SCE. The percentage reduction in area increased with increase in potential in the negative direction.

So far only transgranular cracking was reported in nitrite environment and Sieradzki et al. [37] reported that crack stopped growing when the dynamic strain was stopped. Recently, Mori et al. [42] reported the intergranular cracking of copper in nitrite solution for the first time. Interestingly, the reported stress levels were lower than the yield point and they observed cracking in a constant load test. All the specimens were covered with a black oxide layer at the surface, Auger electron spectroscopy showed film composition was 50 at. % copper and 36 at. % of oxygen. X-ray diffraction analysis revealed the presence of metallic copper, cuprite and tenorite. Cracks were found only in the tube section exposed to the mist of nitrite solution. The fracture surface also showed some oxide formation. Cracking was only observed when the copper tubes were heated from inside and forming a mist above the solution level, when the solution was purged by hydrogen. Similarly, cracking was only observed at more anodic potentials (> 100 mV vs. SCE), where the copper oxide formation was feasible. The authors argue that in metals like copper, which have high stacking fault energy intergranularity is dominant. So at stress level close to yield point in the corrosive environment favor intergranular SCC. The high stress or dynamic straining leads to the continuous slipping and anodic dissolution of planes with low indices and planar dislocation structure results in a transgranular cracking. Interestingly, the cracking conditions mentioned in this work favors the ammonia formation and the authors have confirmed the presence of ammonia too. So this intergranular cracking in nitrite environment could be ascribed to the presence of ammonia, because in the
conditions where transgranular cracking in nitrite solutions have been reported there was no ammonia formation.

2.10 Sulfide stress corrosion of Copper and its alloys

K. Habib and A. Hussain [43] conducted SCC tests on 90Cu-10Ni and 70Cu-30Ni in aerated seawater polluted by sulfides. The concentration of the sulfides ranged from 200 to 3120 ppm. They used a strain rate of $10^{-6}$ s$^{-1}$ since this rate led to realistic test duration without neglecting effects of corrosion reaction. The susceptibility of SCC was determined by comparing the ratio of ultimate tensile stress, percentage elongation and time to failure of samples tested in sulfide polluted sea water to those tested in air. The degree of susceptibility to SCC was almost independent of sulfide concentration and temperature. So the optical examination of the fractured surface was considered as the best method to determine the severity of SCC in each sample. In case of 70Cu-30Ni, the severity of the cracking increased with increase in sulfide concentration at 25$^\circ$C and the most severe cracking was observed at 3120 ppm of sulfide. However, at high temperature the severity of cracking decreased, even at high sulfide concentration. This was ascribed to the lower stability of sulfides at aerated seawater at high temperatures (i.e 50 or 70$^\circ$C). This was not the case in 90Cu-10Ni, where all the samples failed by mild cracking irrespective of the sulfide concentration or temperature.

E. A. Ashour [44] studied the effect of sulfide concentration on the stress corrosion performance of the copper aluminum alloy in seawater. In this case also all the tests were carried out in aerated seawater. In presence of sulfide ions, the protective oxide film was replaced by less
protective Cu$_2$S and the X-ray diffraction analysis confirmed the presence of Cu$_2$S. The sulfide film permitted rapid ionic and electronic transport through it; this made the Cu$_2$S film less protective. The susceptibility of alpha aluminum bronze to SCC increased with increasing sulfide concentration. Similarly, the severity of cracking increased, when the applied potential was increased anodically. The measured high current density at anodic potentials during straining indicated metal dissolution reaction. The decrease in current density values in unstressed specimen indicated the formation of a protective film. The interaction of the applied stress with the oxide film led to the formation of a slip step that resulted in cracking of the film. The results indicated that under open circuit/cathodic potentials copper alloy was less susceptible to SCC, when compared to the anodically polarized specimen. So the cracking mechanism was assumed as film rupture and anodic dissolution at slip steps at high anodic potentials.

S. M. Sayed et al. [45] investigated the SCC behavior of Al-brass and 90Cu-10Ni alloys in sulfide polluted salt water at open circuit potential. Strain rate of $3.5 \times 10^{-6}$ s$^{-1}$ and sulfide concentration in the range of 0 to 1000 ppm were used for the experiment. The fracture toughness was calculated by measuring the area under the stress strain curve. Beyond 500 ppm of sulfide, there was a considerable reduction in the maximum stress, toughness, as well as the time of failure. Metallographic investigation of the fractured surface revealed that below 500 ppm, the failure was a ductile similar to that occurred in air. At 1000 ppm of sulfide, the secondary cracks became more intense in both the alloys. The fracture mode of Al-brass was mixed mode of intergranular and transgranular with intensive secondary cracks at the exposed surface. In case of 90Cu-10Ni, it was predominantly intergranular but there were no intense secondary cracks on the exposed surface. From these observations, the authors suggested that
SCC mechanism of Al-brass in saltwater at high sulfide concentration was film rupture. The intensive micro cracks at the exposed surface supplies a new bare surface in the presence of the stress. This new surface was then attacked by the solution that in turn resulted in propagation of the cracks. However in case of 90Cu-10Ni, the SCC mechanism was sulfide induced cracking or sulfide stress corrosion cracking according to the nature of the formed films namely Cu$_2$S and Cu$_2$O. These films were thick brittle, porous and less adherent. As a result, it was easier to initiate cracking from the corrosion pits.

A. El Domiaty and J. N. Alhaji [46] worked on the susceptibility determination of 90Cu-10Ni alloys to SCC in seawater polluted by sulfide ions. They also found that the density and the distribution of secondary cracks with an increase in sulfide concentration. Similarly, percentage elongation and time to failure decreased with increasing concentration of sodium sulfide. These parameters were considered as an excellent indicator of susceptibility of SCC. The adsorption of the HS$^-$ ions created a negative potential that in turn accelerated the hydrogen discharge reaction, as a result hydrogen evolution was proposed as the possible cathodic reaction. The open circuit potentials increased from their initial active values in noble direction during the slow strain rate test. This behavior was ascribed to the increase in mild crack velocity. However at high sulfide level, this was independent of its concentration. The premature failure of the specimen in high sulfide environment was attributed to the significant increase of hydrogen charging and the associated embrittlement effect. At low sulfide concentrations the contribution of hydrogen was minimal and the crack propagation was associated with the action of sulfide and its oxidation products. The presence of stress resulted in the rupture of the corrosion product film thus
enhancing sulfide stress cracking associated with the anodic dissolution. Optical examination of the fractured specimen revealed that with increasing sulfide concentration, the corrosivity of the environment increased as a result secondary corrosion cracks on the surface also increased. These secondary cracks were completely intergranular and oriented to the direction of the applied stress.

Recently, Taniguchi and Kawasaki [14] reported the intergranular cracking of pure copper in sulfide polluted synthetic seawater at 80°C. The sulfide concentrations ranged from 0.001M to 0.01M and the samples were strained at a constant extension rate of 8.3 x 10^{-7} s^{-1}. The electrode potential was fixed at the rest potential value that was measured in N2 atmosphere under the same conditions before slow strain rate test. The measured rest potentials were -450 mV vs. SCE for 0 M; -880 vs. SCE for 0.001 M, -920 mV vs. SCE for 0.005 M and -950 mV vs. SCE for 0.01 M. The test solutions were refreshed every few days, 3 days maximum, during straining to avoid decrease in sulfide concentration. The influence of sulfide concentration was not apparent up to 0.005 M, but at high concentrations typically 0.01 M of sulfide, there was a distinct decrease of maximum stress and the final strain value. On the SEM examination of fractured surface, few interesting things were observed. No cracks or selective metal dissolution were found in tests that were conducted on the silicone oil and in 0 M sulfide solution. At 0.005 M sulfide some crevasses near fractured surface were observed and in 0.01 M sulfide, numerous obvious cracks were found. The cross section of the fractured specimens revealed the initiation of micro cracks in 0.001 M solutions and a concave pitting was observed at 0.005 M solution. Typical intergranular cracks propagating along grain boundaries were seen in the test involving 0.01 M sulfide solution. Based on these results, it was concluded that the phosphorous deoxidized copper
was susceptible to intergranular attack by sulfide such as selective dissolution at low concentrations and SCC at high concentrations. It was also suggested that the threshold sulfide concentration for SCC initiation was in the range 0.005 to 0.01 M under these conditions. Though only the cracking was reported in this work, the effect of microstructure, temperature and potential on crack initiation and propagation were not studied. Similarly, the mechanism behind the intergranular cracking was not discussed too. So we took this paper as our starting point to probe more on this less understood phenomenon.
3.1 Materials and Sample Preparation

Cylindrical tensile samples were machined from different parts (lid center, lid edge, and tube section) of oxygen free phosphorus doped high pure (99.992% Cu, 45 ppm P, 2 ppm Fe and 1.5 ppm O), copper canisters from SKB (Swedish nuclear fuel and waste management company) Stockholm, Sweden. The dimension of the tensile sample, which was used in the slow strain rate test (SSRT), is shown in Figure 5. The gage length of the sample was abraded to a 1200 grit finish using silicon carbide paper. After abrading, the gage length was masked with an insulating lacquer exposing a surface area of 1 cm². This was done to minimize the sulfide consumption during a 5 day SSRT experiment. For the electrochemical experiments, square samples of 1 cm² area were cut from 2 mm thick copper (99.99% pure, Alfa Aesar) sheets and soldered to a copper wire. Then the samples were mounted in epoxy and abraded to 1200 grit finish, followed by an electropolish in 10 M phosphoric acid. A DC voltage of 1.5 V was applied vs. copper cathode for 2 min.

3.2 Solution Preparation

The electrolytes for all the experiments were made from de-ionized water with a resistivity of 18.2 MΩ cm. Synthetic seawater was prepared by dissolving 30 g of Crystal Sea® Marinemix in one liter of de-ionized water. Similarly different concentrations of sulfide solutions were prepared by dissolving appropriate amount of sodium sulfide (Na₂S anhydrous, 100% purity,
Alfa Aesar). The synthetic seawater had an initial pH of 8.3 but when 10 mM Na$_2$S was added the pH increased to 10.05. For the lower chloride concentration solution, 100 mM sodium chloride was used. The pH increased to 12 when 10 mM of Na$_2$S was added, so the pH was re-adjusted to 10.05 by adding hydrochloric acid for impedance measurements. The observed lower pH in synthetic seawater was due to its buffering capacity.

![Figure 5: Schematic representation of the SSRT specimen. Unit: Inch.](image)

Table 1 Chemical composition of synthetic seawater from Crystal Sea® Marinemix salt package

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration (mM)</th>
<th>Elements</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>524</td>
<td>HCO$_3^-$</td>
<td>2.4</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>452</td>
<td>Sr$^{2+}$</td>
<td>0.14</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>27.1</td>
<td>CO$_3^{2-}$</td>
<td>0.17</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>53.7</td>
<td>Br$^-$</td>
<td>0.075</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>10.2</td>
<td>BO$_3^-$</td>
<td>0.075</td>
</tr>
<tr>
<td>K$^+$</td>
<td>9.7</td>
<td>F$^-$</td>
<td>0.079</td>
</tr>
</tbody>
</table>
Solutions were purged with pure nitrogen for 1 h before addition of the sulfide. The pH of the solution was measured using a digital pH meter from Denver Instruments. All pH and molarities mentioned are measured at room temperature.

3.3 Slow Strain Rate Test (SSRT)

Tensile samples were strained at a rate of $1 \times 10^{-6} \text{ s}^{-1}$ in air and in synthetic seawater containing different concentrations of sodium sulfide (5 and 10 mM) both at room temperature and at 80$^\circ$C, using a CORTEST slow strain rate testing system. During all the experiments the samples were preloaded to 70 MPa before addition of sulfide. The tests were carried out in custom made 300 ml SSRT cell containing the ports for deaeration, counter and reference electrodes. Solution was not refreshed for room temperature test but it was refreshed for high temperature test once in every two days, due to the instability of the sulfides. All tests were done at open circuit potential unless otherwise mentioned.

3.4 Electrochemical Testing

All the electrochemical tests were carried out in a high impact resistance Pyrex cell. The cell had ports for gas purging, reference and counter electrodes. A saturated calomel reference electrode (SCE) and platinum wire counter electrode was used. The SCE measured 45 mV vs. Silver/silver chloride/satd. KCl. All potentials are mentioned with respect to SCE. The electrochemical experiments were carried out in Gamry Femtostat and Princeton PARSTAT 2273, software controlled electrochemical system.

*Electrochemical Impedance Spectroscopy*

An AC potential signal of ±10 mV vs. corrosion potential ($E_{corr}$) over the frequency of 100 kHz
to 100 mHz was used for impedance studies. For the stirring experiments, the following schematic procedure was adopted. Impedance was measured at points A to F; stirring was switched on and off periodically, as indicated in the Figure 6.

**Figure 6: Illustration of the experimental procedure for the stirring experiment.**

*Potentiodynamic Polarization:*

For the voltammetry experiments, a scan rate of 1 mV/s was used in the potential range -1.2 V to 0.1 V vs. SCE.

**Figure 7: Schematic illustration of the gold microelectrode experiment**
Gold microelectrode probe:

The gage length of the tube section tensile specimen was cut and mounted in epoxy. The epoxy mould was grounded until the copper surface was exposed. Then it was immersed in concentrated (50% by volume) HNO₃ for 30 min to form a cavity. A gold microelectrode (0.25 mm diameter) was placed approximately 5 mm from the copper surface of the cavity as shown in the Figure 7. The whole setup was then placed in 300 ml beaker containing synthetic seawater. After purging with nitrogen for one hour, 10 mM Na₂S was added to the solution. The gold microelectrode was connected to the working electrode lead of the potentiostat and voltammetric measurements were carried out. A scan rate of 50 mV/s was used in the potential window of -1.2 to 0.1 V vs. SCE. A separate voltammetry scan was carried out under same conditions in the absence of the copper cavity mould.

3.5 Fracture Surface Examination

After the completion of SSRT tests, the samples were washed thoroughly with de-ionized water. The fractured surface was examined before the removal of the sulfide film under optical microscope. The sulfide film was removed by immersing in 10 M phosphoric acid solution for 20 seconds and the samples were thoroughly rinsed once again in de-ionized water. Then the samples were examined under scanning electron microscope (SEM). For the longitudinal cross section analysis, the fractured specimen was mounted in epoxy. The surface was grounded in various grades of silicon carbide paper and polished to 3 µm finish. Then the polished surface was etched in (50% by volume) nitric acid for 5 seconds and was examined in optical microscope.
RESULTS AND DISCUSSION

4.1 SSRT at Room Temperature

(a) *Lid center specimens*:

A nominal strain rate of $1 \times 10^{-6} \text{ s}^{-1}$ was used for this experiment. The strain rate was calculated by dividing the extension rate by the gage length of the specimen. The tests were carried out in air and in synthetic seawater containing 5 mM and 10 mM of Na$_2$S at room temperature. The corrosion potential was measured with respect to the SCE and the solution was not refreshed during the course of the experiment. The strain was calculated by dividing the difference between the initial and the measured stroke by the gage length. Figure 8 shows that with the increase in sulfide concentration, the final strain value decreases. Similarly the ultimate tensile strength values also decrease with increase in sulfide concentration but not as significantly as in the case of strain. The open circuit potentials started increasing in the positive direction during the course of the experiment. No cracks were found during the examination of the fractured specimen under SEM. Longitudinal cross section of the specimen also did not show any localized attacks on grain boundaries (Figure 10).
(b) Lid edge:

For this experiment, specimens from the lid edge of the canister were used. The extension rate was $1 \times 10^{-6} \text{ s}^{-1}$ and the tests were carried out in synthetic seawater containing 5 and 10 mM Na$_2$S (Figure 9). The solution was not refreshed during the course of the experiment. The open circuit potential profile was identical to that of the lid center specimen. In this case also the final strain values decreased with increase in sulfide concentration. In case lid center specimens the final strain values ranged from 58 to 59 % (3 tests) and 59 to 60 % for 10 mM and 5 mM Na$_2$S respectively,
whereas in case of lid edge specimens it was 56 to 57% (3 tests) and 60 to 61% for 10 mM and 5 mM Na₂S respectively. No cracks were found (Figure 10 and 11). The statistical analysis of the final strain and maximum stress values is relatively immaterial, because the objective behind the SSRT is to check whether the material is cracking or not under the testing condition.

![Graph showing SSRT results of lid edge specimen in synthetic seawater containing various amounts of sulfides at room temperature.](image)

Figure 9: SSRT results of lid edge specimen in synthetic seawater containing various amounts of sulfides at room temperature.

(c) **Effect of cathodic polarization:**

To study the effect of small cathodic polarization, sample from the lid edge of the canister was used. The sample was polarized to -20 mV vs. copper sheet. This small value was chosen in order
to slightly retard the corrosion rate. The usual strain rate of $1 \times 10^{-6} \text{ s}^{-1}$ was used and the solution was not refreshed during the experiment.

Figure 10: SEM images of the fractured surface (top) and lateral cross section (bottom) of lid center specimens in synthetic seawater containing 5mM Na$_2$S.

In this case, the final strain value was more than the value from the test that was done in 10 mM Na$_2$S at the open circuit potential. No cracks were seen in the fractured specimen and the fracture
morphology resembled a normal ductile fracture. Similarly, no localized attacks were detected in the lateral cross section. This showed that even at a small cathodic polarization, the final strain value increased.

Figure 11: SEM images of the fractured surface (Top) and optical image of the lateral cross section of lid center specimen in synthetic seawater containing 10 mM Na$_2$S.
Figure 12: Effect of small cathodic polarization on the stress-strain curve of lid edge specimen in synthetic seawater containing 10 mM Na$_2$S.

4.2 SSRT at 80°C

(a) At Open circuit potential:

Taniguchi and Kawasaki [14] reported that the pure copper suffered from intergranular SCC in synthetic seawater containing 10 mM Na$_2$S at 80°C. The specimen from the lid center was used for this experiment. The solution composition was same as in Taniguchi experiment. However, the
potential was not controlled and the solution was not refreshed in this experiment. The nominal strain rate of $1 \times 10^{-6}$ s$^{-1}$ was used.

![Figure 13: Side view of fractured surface images of lid edge specimen under slight cathodic polarization in synthetic seawater containing 10 mM Na$_2$S.](image)

The raise in temperature resulted in the reduction of the final strain value (Figure 14). Similarly, the ultimate tensile strength value also decreased with increase in temperature. The morphology of the fractured specimen was also different in this case. However the mode of failure was a normal ductile fracture. The scale-like feature near the fracture surface was due to the breakage of the surface film. Though there was a considerable reduction in final strain and the ultimate tensile
strength value, no cracks were found. This reduction could be attributed to the increase in the corrosion rate at high temperatures. Since the potential was not controlled, the corrosion potential could have shifted to a more anodic potential, this in turn could have accelerated the corrosion rate.

Figure 14: Effect of temperature on the stress strain behavior of the lid center specimen in synthetic seawater containing 10 mM Na₂S.
Effect of applied potential:

Since no cracks were reported in the previous run, where the experiment was carried out in the open circuit potential, three different potentials were chosen in order to study the effects of the applied potentials on the stress-strain behavior of the copper in sulfide polluted seawater at 80°C. Based on the potentiodynamic scan in Figure 16 the potentials were chosen in a way that favored only sulfidation reaction. The solution was refreshed every two days, due to the instability of the sulfides at high temperatures. The potential was turned off during the refreshment process, which lasted for 5 minutes. Figures 16 show the results of the slow strain rate tests, it can be clearly seen that the final strain value decreases with increase in the potential in anodic direction. However there was not a big difference in the ultimate tensile strength values with increase in anodic potentials.
The recorded maximum stress values were less than the values obtained from the test that was done at room temperature. Figures 18, 19 and 20 shows the SEM and optical microscope images of the fractured surface and lateral cross section of the specimens. As we can see, there are no sign of cracks; similarly the lateral cross section examination did not show any selective attacks on the grain boundaries. The reason for the reduction in the final strain values at anodic potentials is attributed to the increase in the corrosion rates.
Figure 17: Effect of anodic potentials in the SSRT of tube section specimen in seawater containing 10 mM Na$_2$S at 80°C.
Figure 18: SEM images of the fractured surface (Top) and lateral cross section (Bottom) of the tube section specimen polarized at -950 mV vs. SCE in seawater containing 10 mM Na₂S at 80°C.
Figure 19: SEM images of fractured surface (Top) and lateral cross section (bottom) of tube section specimen polarized at -900 mV vs. SCE in seawater +10 mM Na2S at 80°C.
4.3 Electrochemical studies

4.3.1 Potentiodynamic polarization

Potentiodynamic polarization studies were carried out in the potential window of -1.2 to 0.1V vs. SCE at a scan rate of 1mV/s. Figure 21 shows the voltammetry behavior of copper in synthetic seawater containing 10 and 20 mM Na₂S at 80°C. With the increase of the potential in anodic direction, the measured current also increased. No characteristic peaks were seen in this potential window, however high current values were recorded beyond -100 mV. This raise in current can be ascribed to the dissolution of the copper to Cu²⁺ ions at high anodic potentials. In fact, black precipitate can be seen at the bottom of the cell at the end of the scan. This could be due to the conversion of dissolved Cu²⁺ ions to Cu₂S. In the potential region of -900 to -100 mV the current remains almost constant, this represent the limiting current region for the sulfidation reaction. Based on the limiting current calculations, a diffusion layer thickness of 180 µm was obtained. Detailed calculations are given in Appendix.

4.3.2 Electrochemical impedance studies

(a) Effect of chloride:

In SSRT experiments, synthetic seawater was used as the base solution. To understand the effect of the high chloride concentration of the seawater in the sulfidation reaction, impedance studies were carried out in solutions containing different concentrations of chloride. Figure 22 shows the
impedance behavior of copper in sulfide containing solution at two different concentrations of chlorides. At lower chloride concentration, the charge transfer resistance values were high compared to the high chloride concentration case. This shows that the corrosion process is very active at high chloride concentrations and also indicates that the sulfide film formed under these conditions are not protective ones.

Figure 21: Potentiodynamic polarization of copper in sulfide-polluted seawater at 80°C.

(b) Immersion studies:

Long time exposure of copper in sulfide containing seawater leads to the emergence of the second time constant in the impedance spectrum as shown in Figures 23 and 24. The charge transfer resistance values decreased with increase in the sulfide concentration and with the immersion time.
The feature in the lower frequency region reflects the properties of a defective surface film offering a mass transfer limitation to the inward diffusion of the corrosive species. Two types of equivalent circuit were used to fit the obtained impedance data (Figure 25).

Figure 22: Nyquist plot showing the effect of chloride concentration on the sulfidation reaction in solution containing 10 mM Na₂S at room temperature. Frequency range: 100 kHz to 0.1 Hz.

Type I circuit was used to fit the shorter immersion (< 15 h) impedance data, while type II circuit was used to fit the longer immersion (>15 h) data (Figure 30). The $R_{\text{film}}$ and CPE$_{\text{film}}$ are the sulfide film’s resistance and constant phase element. The double layer charge transfer resistance and its capacitance are represented by the $R_{\text{ct}}$ and $C_{\text{dl}}$ respectively, while Warburg impedance is
represented by W. Figure 26 show the variation of the equivalent circuit parameters with time in case of 10 mM Na$_2$S concentration. We can clearly see that the films resistance ($R_{\text{film}}$) increases with time, while the constant phase element associated with the film ($CPE_{\text{film}}$) decreases with time.

![Nyquist plot](image)

**Figure 23:** Nyquist plot of tube section specimen immersed in synthetic seawater containing 5 mM Na$_2$S at room temperature. Frequency range: 100 KHz to 0.1 Hz.

However the charge-transfer resistance ($R_{\text{ct}}$) initially increases but after longer immersion it decreases, this is reflected in the trend of the double layer capacitance ($C_{\text{dl}}$) which increases continuously with time. The raise in the film resistance is due to the increase in the thickness of the sulfide film which in turn decreases the constant phase element. Similarly the trend in the charge-
transfer resistance values suggests that the sulfide film is not protective. These results indicate that the corrosion of copper in sulfide polluted synthetic seawater at room results in the formation of a thicker sulfide film. This surface film is not protective in nature as it is indicated by the charge transfer resistance values resulting in continuous corrosion of copper.

Figure 24: Nyquist plot of tube section specimen immersed in synthetic seawater containing 10 mM Na₂S at room temperature. Frequency range: 100 KHz to 0.1 Hz.

Figure 25: Type I (left) and II (right) equivalent circuits that were used to fit the impedance data.
Figure 26: Variation of the equivalent circuit parameters with the immersion time. Solution: synthetic seawater + 10 mM Na$_2$S at room temperature.
(c) *Stirring experiments:*

In potentiodynamic and impedance measurements, the results indicate the existence of a mass transfer limitation process. In order to confirm its presence, the impedance measurements were done, while periodically switching ON and OFF the stirring of the solution. Figure 6 shows the schematic illustration of this experiment. The impedance measurements were done at points A to F, the stirring was switched ON and OFF periodically as indicated in the illustration. Figure 27 shows the results of the impedance measurements.

![Graph](image)

**Figure 27:** Effect of stirring on the impedance behavior of the tube section specimen immersed in synthetic seawater containing 10 mM Na₂S at room temperature. Frequency range: 100 kHz to 0.1 Hz.
Whenever the stirring is turned ON, at points A, E and F the charge transfer resistance decreases dramatically. Similarly, whenever the stirring is turned OFF, at points B, C and D the charge transfer resistance increases. This behavior is in line with the findings of J. Smith (30), in which the measured diffusion limiting anodic currents in the voltammograms approach the theoretical Levich limiting currents only when the electrode rotation rate tends to zero. So we can conclude that the sulfide film offers a mass transport limitation to the inward diffusion of the sulfide ions even at 10 mM concentration of Na₂S.

Figure 28: Cyclic voltammetry on gold microelectrode in synthetic seawater containing 10 mM Na₂S. Scan rate: 50 mV/s.
4. 3. 3 Intermediate detection

The sulfidation reaction of copper occurs without obvious dissolution of the copper ions. J. Smith [30] proposed that the sulfidation reaction of the copper in aqueous solution occurs by the formation of the several solution complexes. In-situ Raman spectroscopy analysis were performed to detect these complexes, however no characteristic peak was obtained. To probe more on this solution complex theory, a microelectrode probe voltammetry analysis was done. A gold microelectrode was placed at a distance of 5 mm from the copper surface in the cavity and cyclic voltammetry was carried out on the gold electrode in synthetic seawater containing 10 mM Na₂S at room temperature. The schematic illustration of the copper cavity is shown in Figure 7. This scan rate was chosen, because the copper sulfide quickly forms when HS⁻ comes in contact with the copper. A potential window of -1.2 to 0.1 V vs. SCE was used for the voltammetry. A separate scan was made in bulk solution for reference. However in both cases a cathodic peak ca. -900 mV vs. SCE. Apart from this no other characteristic peaks were observed.
Chapter 5

SUMMARY AND CONCLUSIONS

The susceptibility of the phosphorus de-oxidized high pure copper to stress corrosion cracking was studied in synthetic seawater containing 5, 10 and 20 mM of Na$_2$S. The influence of the temperature, cathodic and anodic polarization on the susceptibility was also studied. Under the tested conditions, the high pure copper is not susceptible to stress corrosion cracking. In all these cases, the final strain values and ultimate tensile strength values decreased with increase in the sulfide concentration, anodic potentials and the temperature. This trend could be due to the acceleration of the corrosion reaction by these three factors. The probable reasons for the absence of cracking are

- The corrosion of copper in sulfide-polluted seawater is of a uniform type. The slip dissolution model requires an active path for the initiation and propagation of the crack. However the metallographic examination of the fractured surface and the lateral cross section did not show any form-localized attack such as pitting and intergranular attack, which is a potential active path.

- The sulfide film is not a protective film like an oxide film. From the impedance measurements we can see that the charge transfer resistance values decrease with increase in sulfide concentrations and also with the increase in the immersion time. The high chloride concentration also makes the surface very active. Most of the SCC models require a protective film for cracking. This is because, for the propagation the corrosion rate at the
crack tip should be higher than the crack walls as shown in the following figure. \( M_T \) is the corrosion rate at the crack tip and \( M_W \) is the corrosion rate at the walls of the crack. For the propagation of the crack \( M_W/M_T<1 \).

![Diagram]

• The potentiodynamic polarization and long time impedance studies indicate the presence of a mass transfer limitation process. The stirring experiments confirm its presence. Based on these results we can conclude that the sulfide film on the copper surface is a defective one and also offers a mass transfer limitation to the inward diffusion of the sulfide ions. The corrosion process should be under activation or charge transfer control for SCC. If the corrosion process is under diffusion control, then the corrosive species will not reach the crack tip. This results in the blunting of the crack tip.
Future work

• To pre-crack the copper specimen in another environment and carry out slow strain rate test in sulfide environment. This would give information about the crack propagation in sulfide environment.

• To carry out more SCC testing at different strain rate and in near-neutral pH.

• To carry out in situ synchrotron experiment to probe more on the copper sulfidation reaction.

• To develop a simple model with realistic crack geometry, for the limiting crack growth possible by dissolution.
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APPENDIX

Diffusion Layer thickness calculations:

\[ i_{\text{lim}} = \frac{nFDC_{\text{BULK}}}{h} \]

Where, \( h \) is the thickness of diffusion layer (cm); \( n \) is the number of electrons transferred; \( F \) is the Faraday number (C/mol); \( C_b \) is the bulk concentration of the species (mol/1000 cm\(^3\)); \( i_{\text{lim}} \) is the limiting current density (A/cm\(^2\)).

From the Figure 29, an average limiting current value of 1.45 mA/cm\(^2\) was obtained for the sulfidation reaction of copper in synthetic seawater containing 10 mM Na\(_2\)S at room temperature. For \( D_{\text{HS}} = 1.37 \times 10^{-5} \text{ cm}^2/\text{s} \) [47], \( n= 2 \), \( C_{\text{Na}_2\text{S}} = 10 \text{ mM} \) and \( F= 96500 \text{ C/mol} \) a diffusion layer thickness of 180 \( \mu \text{m} \) is obtained.
Figure 29: Potentiodynamic polarization of tube section of copper in synthetic seawater containing 10 mM Na₂S at room temperature. Scan rate: 1 mV/s.
MASS TRANSFER LIMITATION

Our limiting current calculation yielded a diffusion layer thickness of 180 microns. This is higher than the nominal value that is around 50 to 75 microns. We used the following equation, which do not take into account of the diffusion through the porous surface film.

\[ i_{lim} = \frac{nFD}{C_{BULK}} \frac{C_{BULK}}{h} \]

Where \( i_{lim} \) is the limiting current density, \( n \) is the number of electron transfer, \( D \) is the diffusion coefficient of HS\(^{-}\) and \( C_{BULK} \) is the bulk concentration and \( h \) is the thickness of Nernstian diffusion layer. But in actual condition the sulfide film offers a mass transfer limitation to the inward diffusion of the sulfide ions, so we’ve to consider the mass transfer through the film also. So the offset from the nominal value is due to the formation of the porous film. The following is an extended version of the above equation.

A: Region between the electrode surface (Cu) and the sulfide film (Cu\(_2\)S)

B: Region between Nernstian diffusion layer and the bulk.
Flux in region A ($J_1$):

$$J_1 = D_1 \frac{(C_{\text{FILM}} - C_{\text{SURFACE}})}{h_1}$$

Flux in region B ($J_2$):

$$J_2 = D_2 \frac{(C_{\text{BULK}} - C_{\text{FILM}})}{h_2}$$

Where, $h_1$ and $h_2$ are the thickness of the porous film and Nernstian diffusion layer. Similarly $D_1$ and $D_2$ are the diffusion coefficient of HS$^-$ in Cu$_2$S film and the solution respectively.

Total flux: $J_1 + J_2 =

$$J_{\text{TOTAL}} = D_1 \frac{(C_{\text{FILM}} - C_{\text{SURFACE}})}{h_1} + D_2 \frac{(C_{\text{BULK}} - C_{\text{FILM}})}{h_2}$$

Under limiting current conditions $C_{\text{SURFACE}} = 0$. So the above equation becomes

$$J_{\text{TOTAL}} = \frac{(h_1 D_1 - D_2 h_1)}{h_1 h_2} C_{\text{FILM}} + D_2 \frac{(C_{\text{BULK}})}{h_2}$$
Figure 30: Equivalent circuit fit for the impedance data of tube section of copper immersed in synthetic seawater containing 10 mM Na₂S at room temperature. Frequency: 100 kHz to 0.1 Hz.
### SLOW STRAIN RATE TEST (SSRT) IN 0.1 M NaCl:

Table 2: List of SCC tests that were carried out using lid center specimens.

<table>
<thead>
<tr>
<th>Test no.</th>
<th>Notes</th>
<th>Solution composition</th>
<th>Temperature</th>
<th>Extension rate</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>The test was stopped after 5% plastic straining.</td>
<td>Na$_2$S = 5 mM Cl$^-$ = 100 mM pH = 11.5</td>
<td>Room Temperature</td>
<td>1.e-7 s$^{-1}$</td>
<td>No sign of crack initiation</td>
</tr>
<tr>
<td>2</td>
<td>The sample was fractured</td>
<td>Na$_2$S = 5 mM Cl$^-$ = 100 mM pH = 11.5</td>
<td>Room Temperature</td>
<td>1.e-6 s$^{-1}$</td>
<td>No cracks; only uniform type of corrosion.</td>
</tr>
<tr>
<td>3.</td>
<td>The pH was adjusted to 8.5 using HCl and the sample was fractured.</td>
<td>Na$_2$S = 5 mM Cl$^-$ = 100 mM</td>
<td>Room Temperature</td>
<td>1.e-6 s$^{-1}$</td>
<td>No cracks; only uniform type of corrosion.</td>
</tr>
<tr>
<td>4</td>
<td>The test was stopped after 5% plastic straining.</td>
<td>Na$_2$S = 10 mM Cl$^-$ = 100 mM pH = 12</td>
<td>Room Temperature</td>
<td>1.e-7 s$^{-1}$</td>
<td>No sign of crack initiation</td>
</tr>
<tr>
<td>5</td>
<td>The sample was fractured</td>
<td>Na$_2$S = 10 mM Cl$^-$ = 100 mM pH = 12</td>
<td>Room Temperature</td>
<td>1.e-6 s$^{-1}$</td>
<td>No cracks; only uniform type of corrosion.</td>
</tr>
<tr>
<td>6</td>
<td>The pH was adjusted to 8.5 using HCl and the sample was fractured.</td>
<td>Na$_2$S = 10 mM Cl$^-$ = 100 mM pH = 12</td>
<td>Room Temperature</td>
<td>1.e-6 s$^{-1}$</td>
<td>No cracks; only uniform type of corrosion.</td>
</tr>
<tr>
<td>7.</td>
<td>The sample was fractured</td>
<td>Na$_2$S = 20 mM Cl$^-$ = 100 mM pH = 12</td>
<td>Room Temperature</td>
<td>1.e-6 s$^{-1}$</td>
<td>No cracks; only uniform type of corrosion.</td>
</tr>
</tbody>
</table>

Optical microscope images:
Figure 31: Optical microscope images of exposed surface of lid center specimens after 5 % plastic strain in 0.1 M NaCl solution containing 5 mM Na₂S (left) and 10 mM Na₂S (right). Magnifications 4X.

Figure 32: Optical microscope images of side view of fractured surface of lid center specimens in 0.1 M NaCl solution containing 5 mM Na₂S (left) and 10 mM Na₂S (right). Magnifications 4X.
Scanning Electron Microscope Images

Figure 33: SEM images of side view of fractured surface of lid center specimens in 0.1 M NaCl containing 10 mM Na₂S (left) and 20 mM Na₂S (right).