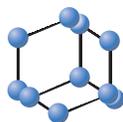


RESEARCH ARTICLE

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The Mechanism of Sulphide Film Growth on Copper in Anaerobic Sulphide Solutions Under Natural Corrosion Conditions



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Abstract: Background and Method: The growth mechanism of sulphide films formed on copper in anaerobic 0.1 M NaCl + 5×10^{-4} M Na₂S solution has been investigated under natural corrosion conditions for exposure periods up to 1691 hours using scanning electron microscopy, focused ion beam cross-sectioning, and a Au marker procedure.

Results and Conclusions: The film formed by a chemical deposition process via an outward growth mechanism. This process was controlled by cuprous ion transport in the film combined with sulphide diffusion in solution.

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1. INTRODUCTION

Since copper is stable under aqueous anaerobic conditions, it is a primary candidate material for the fabrication of high level nuclear waste containers to be placed in deep geologic waste repositories. Once the oxygen trapped in the groundwater on repository closure is consumed, the only available oxidant would be sulphide, present in groundwater due to either mineral dissolution (*i.e.* pyrite, FeS₂) or produced by the action of sulphate reducing bacteria. Corrosion would then be controlled by either the diffusive transport of sulphide through the compacted clay buffer surrounding the canister, or by the expected protective properties of the copper sulphide layer on the canister surface [1]. This makes a knowledge of the growth mechanism of the sulphide film formed on the copper surface under natural corrosion conditions essential for the performance assessment of copper nuclear waste canisters under deep geologic repository conditions.

While studies on copper corrosion in anaerobic sulphide solutions under either electrochemically-controlled [2-7] or natural corrosion conditions [1, 8, 9] indicate that the sulphide film formed on Cu in aqueous sulphide solutions grows at the film/solution interface, direct experimental evidence has not been presented. In this paper, we use a Au-marker procedure coupled with scanning electron microscopy (SEM) on corroded surfaces and focused ion beam (FIB) cut cross sections, to determine the sulphide film growth mechanism on copper corroding in anaerobic aqueous sulphide solutions.

2. EXPERIMENTAL PROCEDURES

Experiments were conducted using phosphorous-doped (40-60 ppm), oxygen-free copper provided by the Swedish Nuclear Fuel and Waste Management Co. (SKB), Stockholm, Sweden. The working electrode was a copper disk, with a diameter of 1 cm, threaded into a stainless steel shaft. The electrode and shaft were painted with non-conductive lacquer to prevent contact of the Cu/steel junction with the aqueous solution. After painting, the electrode was heated at 60°C for 12 h to promote adhesion between the paint and the sample. The exposed Cu surface was polished successively with 240, 600, 800, 1000, 1200 grade SiC paper and then to a mirror finish using 1 μm, 0.3 μm, and 0.05 μm Al₂O₃ suspensions. Prior to experiments, the electrode was washed with Type I water (resistivity of 18.2 MΩ·cm) purified using a Millipore-Q plus unit, ultrasonically cleaned in methanol, washed again with Type 1 water, and finally dried using argon gas.

All experiments were performed within an argon purged anaerobic chamber (Canadian Vacuum Systems Ltd.) maintained at a positive pressure (2-4 mbar) by an MBraun glove box control system to ensure anoxic conditions. The oxygen concentration in the chamber was analyzed with an MBraun oxygen probe with a detection limit of 1.4 mg/m³. The anaerobic chamber was maintained at a total oxygen concentration ≤ 4.2 mg/m³, which includes the oxygen in both air and vapor. The actual oxygen content of the solution would have been less than this value. Even though a trace amount of oxygen may have been present, copper sulphide is more stable in an aqueous sulphide solution than copper oxide based on thermodynamic data ($\Delta G^\circ = -101.46$ kJ/mol for the conversion of Cu₂O to Cu₂S in sulphide solutions at 298 K [10]:

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$\text{Cu}_2\text{O} (\text{s}) + \text{HS}^- (\text{aq}) \rightarrow \text{Cu}_2\text{S} (\text{s}) + \text{OH}^- (\text{aq})$ and available literature [4, 11-13].

The 0.1 M NaCl + 5×10^{-4} M Na_2S solution (pH = 9.96) was prepared with Type I water, reagent-grade sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 98.0% assay), and analytical-grade sodium chloride (NaCl, 99.0% assay). The sodium chloride was added to simulate the saline groundwater conditions anticipated in a repository.

Since exposure periods were long, the $[\text{SH}^-]$ was monitored weekly by measuring the pH as described previously [9], and SH^- added to readjust the $[\text{SH}^-]$ to its original value. Experiments were performed at $25 \pm 2^\circ\text{C}$. The specimen was immersed in anoxic 0.1 M NaCl + 5×10^{-4} M Na_2S solution (1 L) for various times under natural corrosion conditions. A standard three-electrode system was employed with a Pt plate as the counter electrode and a saturated calomel reference electrode (SCE). All potentials are quoted on the SCE scale (+0.241 V/NHE). Prior to the experiment, the specimen was cathodically cleaned at -1.6 V/SCE for 2 minutes, and then at -1.15V/SCE for 2 minutes to allow the detachment of hydrogen bubbles formed by water reduction at the lower potential.

After 161 h of immersion to form a thin sulphide film on the copper surface, the specimen was removed from the solution, washed with Type I water, dried using cold high-purity argon gas. A Au line (width ~ 200 μm ; thickness ~ 100 nm) was then sputter-deposited on the surface of the sulphide film to act as a marker. The Au-marked specimen was then re-immersed in the same solution for a further ~ 1530 h for a total exposure period of 1691 h (~71 days). The electrode was then removed from the solution, rinsed with Type I water for 10 minutes, and dried with cold Ar gas. Analyses of the surface were then performed after a minimum period of interim storage (< 30 minutes). The surface and cross-sectional morphologies of the corroded specimen were observed using a Leo 1540 FIB/SEM microscope (Zeiss Nano Technology Systems Division, Germany). The composition of the sulphide film was qualitatively analyzed by Energy Dispersive X-ray analysis (EDS) using a Leo 1540 FIB/SEM microscope.

3. RESULTS AND DISCUSSION

We have shown previously [9] that the sulphide film formed on a copper surface in anoxic 0.1 M NaCl + 5×10^{-4} M Na_2S solution under natural corrosion conditions was a single layer Cu_2S (chalcocite) film. After 161 h immersion, this film had an average thickness of ~ 200 nm with previous experiments showing that, for extended immersion times (up to 1691 h), the film growth kinetics obeyed a parabolic law, suggesting a diffusion-controlled process.

In a 0.1 M NaCl + 5×10^{-4} M Na_2S solution, the $\text{SH}^-/\text{S}^{2-}$ buffer couple makes the pH of the solution a function of the S^{2-} concentration in the solution [14]. During the Au marker test, the pH of the solution was stable, indicating SH^- depletion in the solution did not occur. Since the diffusion coefficient of SH^- in solution ($1.731 \times 10^{-5} \text{ cm}^2/\text{s}$ [15]) is about five orders of magnitude larger than that of Cu^+ in Cu_2S film ($\sim 10^{-10} \text{ cm}^2/\text{s}$ [9, 10]), it is unlikely that the growth of the sulphide in this solution is totally controlled by SH^- diffusion

in the solution. Under the parabolic growth law observed, film growth could be controlled by either SH^- or Cu^+ diffusion within the film. If sulphide transport within the film was dominant, film growth would occur at the metal/film interface; *i.e.*, *via* an inward growth mechanism. Consequently, on re-immersion of the Au-marked specimen, growth would occur under the film with the Au remaining exposed on the sulphide film surface, as illustrated in Fig. (1a).

By contrast, film formation *via* an outward growth mechanism at the film/electrolyte interface would require Cu^+ transport from the metal surface to the film/solution interface and film growth after re-immersion would bury the Au marker. Moreover, the thickness of the film below the Au marker, that was grown prior to the deposition of the Au, would not increase, as illustrated in Fig. (1b).

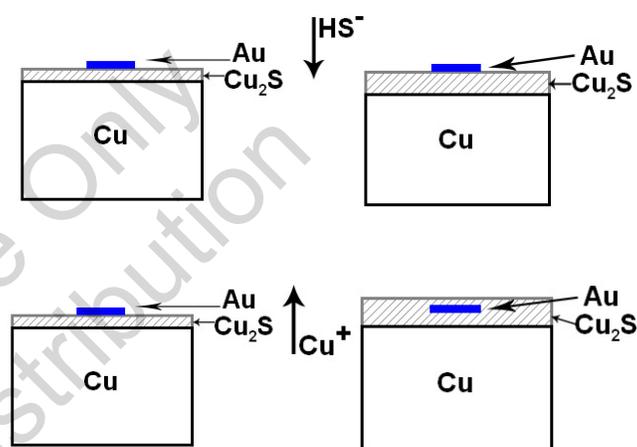


Fig. (1). Schematic of sulphide film growth mechanism: (a) inward growth mechanism if corrosion film growth is controlled by SH^- diffusion in film; (b) outward growth mechanism if corrosion film growth is controlled by Cu^+ diffusion in film or by Cu^+ diffusion in film combined with SH^- diffusion in solution from bulk solution to the film/solution interface.

After a total immersion time of 1691 h, surface and cross-sectional morphologies of the Au-marked copper specimen were recorded, Fig. (2) and Fig. (3), respectively. Fig. (2) shows that an abundance of crystalline particles accumulated on the sulphide film indicating film growth on re-immersion occurred *via* chemical deposition not *via* solid state transport through a thickening film.

The FIB-cut cross sections, Fig. (3), show that the Au marker was buried by this deposition process while the thickness of the film beneath the Au marker remained similar to that of the pre-formed film before the deposition of the marker (~ 200nm). This confirmed that an outward film growth occurred, a process requiring a combination of Cu^+ diffusion within the film and SH^- diffusion in the solution. Our previous work [9, 16] demonstrated that SH^- diffusion in a solution containing this concentration of sulphide partially contributed to film growth, confirming an outward growth mechanism controlled by a combination of Cu^+ diffusion in the film and SH^- diffusion in solution.

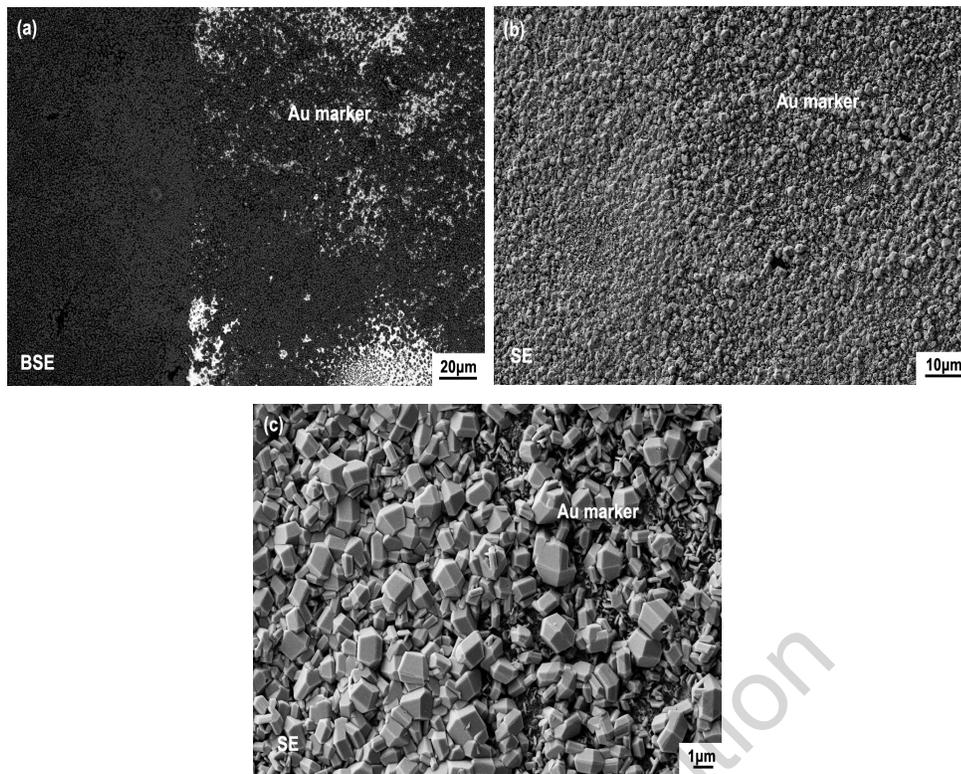


Fig. (2). Surface morphology of oxygen-free copper after immersion in 0.1 M NaCl + 5×10^{-4} M Na₂S solution for total of 1691 h (161 h prior to deposition of the Au marker + 1530 h afterwards); SE: secondary electron detection, and BSE: back-scattered electron detection.

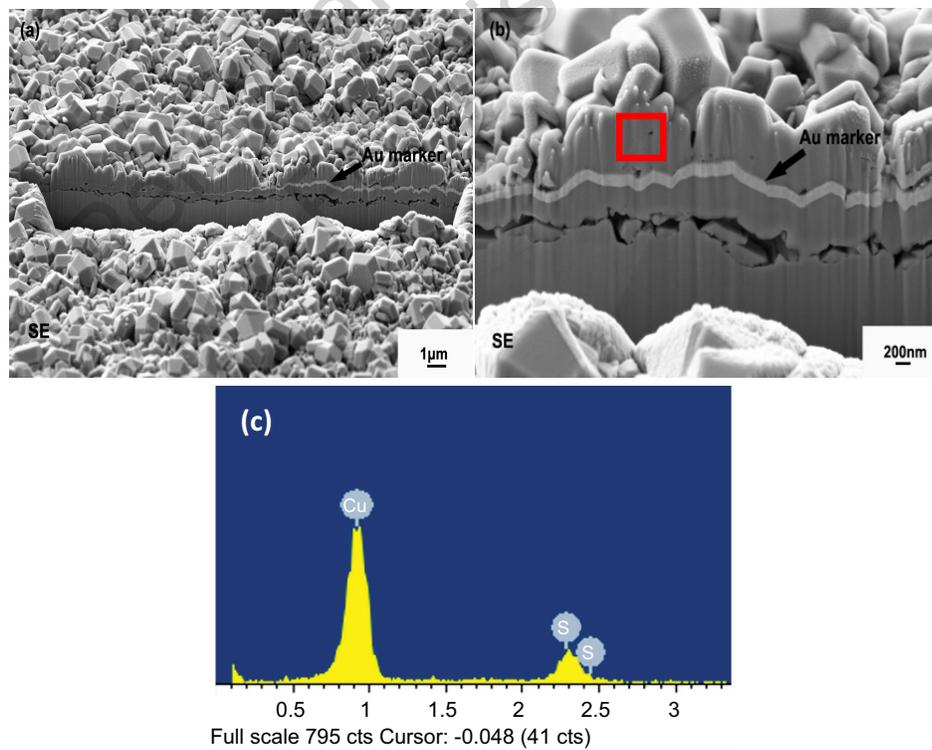


Fig. (3). Cross-sectional morphologies of oxygen-free copper cut using FIB after immersion in 0.1 M NaCl + 5×10^{-4} M Na₂S solution for total of 1691 h (161 h prior to deposition of the Au marker + 1530 h afterwards) [16].

Figs. (2, 3a and 3b) also show that the Cu_2S particles deposited above the Au layer, and analyzed using EDS (Fig. 3c), were similar to those deposited generally across the surface and that the film thickness was effectively uniform after immersion, regardless of whether the surface was covered with sputtered Au or not. Since the diffusion coefficient for Cu in a Au single crystal is much smaller ($\sim 10^{-17}$ cm^2/s at room temperature [17]) compared to that in the sulphide film ($\sim 10^{-10}$ cm^2/s [9, 10]), film growth at locations above the Au layer could not have been sustained by Cu transport through the Au only by the lateral transport from areas not covered by Au. The Cu underneath the Au marker will diffuse through the pre-grown sulphide film, and then transport along the pre-grown sulphide film/Au marker interface to react with sulphide in bulk solution and form $\text{Cu}(\text{SH})_2^-$ complexes and Cu_3S_3 clusters [18, 19]. Compared to Cu diffusion at other regions without Au coverage, the diffusion of Cu along the pre-grown sulphide film/Au marker interface will be much faster, but the diffusion path will be longer. These two factors may make the diffusion time of the Cu at the Au-covered and Au-free regions similar, which accounts for the uniform corroded Cu interface. As we have recently shown, Cu (I) can be transported in a sulphide solution as both $\text{Cu}(\text{SH})_2^-$ complexes and Cu_3S_3 clusters [18, 19], a process that would be much faster than transport through the Au. This would allow lateral transport across the Au surface. Also, since both the Cu_2S film [9] and the Au surface strongly adsorb SH^- [20-24] the precipitation of $\text{Cu}(\text{SH})_2^-$ complexes and Cu_3S_3 clusters would be promoted on both surfaces.

CONCLUSION

Using a Au marker procedure, the sulphide film formed during copper corrosion in a 0.1 M $\text{NaCl}+5\times 10^{-4}$ M Na_2S solution was shown to form *via* an outward growth process involving a chemical deposition process. This process was controlled by a combination of Cu^+ transport within the film and SH^- diffusion in the solution. Copper was transported in the form of either $\text{Cu}(\text{SH})_2^-$ complexes or Cu_3S_3 clusters.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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