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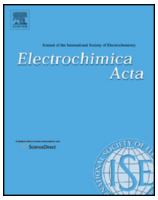

Mechanisms of Film Growth on Copper in Aqueous Solutions Containing Sulphide and Chloride under Voltammetric Conditions

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ABSTRACT

The electrochemical behavior and film formation mechanisms of oxygen-free copper have been studied in aqueous solutions containing a wide range of sulphide and chloride concentrations using rotating disk electrodes and cyclic voltammetry. Scanning electron microscopy, energy dispersive X-ray spectroscopy and focused ion beam techniques were employed to characterize the morphology, composition and structure of the copper sulphide films formed on the copper surface under voltammetric conditions. These studies show that three distinct type of films were formed depending on the sulphide concentration, the flux of sulphide to the electrode surface, and the chloride concentration of the solution. The properties of the film and the mechanism of growth were determined by competition between sulphide diffusion in solution and the rate of interfacial reactions on the Cu surface. Comparison of these properties of electrochemically grown films to those of films grown under corrosion conditions indicates that pitting should not occur under the conditions expected in a nuclear waste repository.

1. Introduction

A key requirement for the continued use of nuclear power is the successful management of the spent nuclear fuel. One approach under study in many countries, including Sweden, Finland and Canada, is permanent disposal of the spent fuel in a deep geological repository (DGR). In such disposal facilities the spent fuel would be placed in canisters, specifically designed to avoid both corrosion and mechanical failure. The container will be fabricated with a carbon steel insert, and an outer shell of copper. It is proposed that these containers be buried in crystalline rock approximately 500 m below the surface and the excavated boreholes backfilled with bentonite clay [1]. Cu is chosen since it should be inert to corrosion in the anoxic environments anticipated in a DGR [1–7]. The Cu layer would be about 50 mm thick and the metal would be O-free and P-doped. Removing the O and doping with small concentrations of P (30 to 100 ppm) improves the creep resistance, thereby limiting the possibility of physical deformation of the container after emplacement [8].

Although Cu is chosen for its thermodynamic resistance to corrosion in anoxic environments, Swedish repositories are known to contain SH^-, produced in the groundwater as a consequence of $SO_4{}^{2-}$-reducing bacteria and mineral dissolution [9]. This is potentially detrimental to the container since SH^- can act as an oxidant for Cu. Container corrosion in the groundwaters anticipated in a repository would also be complicated by the presence of high concentrations of Cl^-.

Previous studies have proposed that Cu corrosion begins with the adsorption of an anion [10] and corrosion in aqueous SH^- solutions involves a similar first step [9],

$$Cu + SH^- \rightarrow Cu(SH)_{ads} + e^- \tag{1}$$

followed by a slow reaction step involving Cu to produce a Cu_2S film, the overall process being supported by H^+ or H_2O reduction [9],

$$Cu + Cu(SH)_{ads} + SH^- \rightarrow Cu_2S + H_2S + e^- \tag{2}$$

In long-term experiments under these conditions a Cu_2S film (chalcocite) was formed. Since Cu_2S formed at a constant rate, the film can be considered only partially protective, and corrosion may also be facilitated by the complexation and solubilization of Cu^I by Cl^- [11],

$$Cu(SH)_{ads} + 2Cl^- \rightarrow CuCl_2{}^- + SH^- \tag{3}$$

Since the solubility product of Cu^I in SH^- solution is very small [9], any dissolved Cu^I would be expected to eventually precipitate as Cu_2S,

$$2CuCl_2{}^- + SH^- \rightarrow Cu_2S + 4Cl^- + H^+ \tag{4}$$

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Kinetic studies revealed two types of growth process dependent on [SH⁻]. At [SH⁻] = 5.0×10^{-4} M growth follows a parabolic law and is governed by the transport of the Cu^+ ion through the Cu_2S matrix or along grain boundaries in the Cu_2S film [9,12]. However, when the [SH⁻] is lower (5.0×10^{-5} M), film growth is controlled by SH^- diffusion, and the kinetics follow a linear growth law leading to a porous non-protective film [12].

A remaining question is whether or not, given that the [Cl⁻] is expected to be high, pitting can occur in saline groundwaters containing SH^-. For this to occur the surface film must be generally passivating with local breakdown sites, and the cathodic reaction, in this case SH^- or H_2O reduction, must be sustained on the passive surface outside the pitting area.

In this paper, a series of voltammetric experiments (alternatively called polarization experiments) were performed in solutions containing a range of [SH⁻] and [Cl⁻]. These studies serve two functions: (i) they provide information on the sulphide film growth process on Cu; and (ii) they enable us to determine when passivation occurs and whether or not this can lead to film breakdown and the initiation of pitting.

2. Experimental

2.1. Electrochemical cell and instrumentation

All electrochemical data were collected using a conventional three-electrode electrochemical glass cell. A Pt sheet rolled into a cylinder was used as the counter electrode and connected to external circuitry by a Pt wire. A standard calomel electrode (SCE, 0.242 V vs. SHE) was used as the reference electrode for all experiments. The cell was housed inside a Faraday cage to reduce electrical noise from external sources. All experiments were conducted using a rotating disc working electrode. The electrode rotation rate was controlled by a Pine Instrument Company Analytical Rotator Model AFA86 Serial 882, and electrochemical measurements were made using a 1287 Solartron potentiostat connected to a computer equipped with CorrWare software.

2.2. Cu composition and preparation

O-free, P-doped Cu provided by the Swedish Nuclear Fuel & Waste Management Co. (SKB), Stockholm, Sweden, was machined into Cu disks. Ti rods were threaded into the back of the discs and the Cu was set into a Teflon holder using an epoxy resin. Only a single flat Cu face with a surface area of 0.785 cm^2 was exposed to solution. Prior to an experiment, the Cu electrode was first ground with a sequence of SiC papers with grit sizes: 1000, 1200, and 4000. Then, to achieve a mirror finish, the electrode was polished with Al_2O_3 suspensions with decreasing suspension size (1 μm, 0.3 μm, and 0.05 μm). The electrode was then rinsed thoroughly with Type I water (resistance: 18.2 MΩ·cm) to remove any polishing residue and dried in a stream of ultrapure Ar gas.

2.3. Solutions

Electrolyte solutions were prepared with Type I water obtained using a NANOPure system. Chemicals were reagent-grade and purchased from Caledon Laboratories Ltd. All water was purged with Ar gas for one hour prior to the preparation of solutions. The actual [SH⁻] used were higher than those anticipated in a repository. The [Cl⁻] were representative of the range of groundwater concentrations anticipated. The NaCl and $Na_2S{\cdot}9H_2O$ concentrations used are listed in Table 1. Since Na_2S was stored in the hydrated form, the crystals were dried before being weighed to minimize error in calculated concentrations. Once in the electrochemical cell, the solution was purged for a minimum of 45 minutes before an experiment to ensure an anoxic environment. Subsequently, the solution was continuously purged with a stream of Ar gas.

Table 1
NaCl and Na_2S concentrations.

NaCl concentration/M	Na_2S concentration/M
0.1	5.0×10^{-5}
0.5	1.0×10^{-5}
1.0	5.0×10^{-4}
3.0	1.0×10^{-3}
5.0	2.0×10^{-3}

2.4. Cyclic voltammetry (CV)

Cyclic voltammetry (CV) was used to investigate the mechanism of sulphide film formation. Prior to applying a voltammetric scan, the electrode was cathodically cleaned at -1.5 V/SCE to remove air-formed oxides, and then at -1.15 V/SCE for a further 60 s. Voltammetric scans were performed from an initial potential in the range -1.15 V/SCE to -1.5 V/SCE to various anodic limits at a scan rate of 2 mV/s. The choice of starting potential had no influence on the subsequent electrochemical behavior.

2.5. Scanning electron microscopy (SEM)

Surface imaging was performed using a LEO (Zeiss) 1540XB FIB/SEM equipped with an Energy Dispersive X-ray Spectroscopy (EDX) analyzer to elucidate the elemental composition of the surface. Analyses were performed at the Western Nanofabrication Facility. Focused ion beam (FIB) cross-sections were prepared using a Ga ion beam. The sample was not pre-coated before a cut was made.

3. Results and discussion

CVs were performed in solutions with various [Cl⁻] and [SH⁻] and at various electrode rotation rates from 0 to 157 rad/s. The anodic and cathodic current responses varied with solution composition, electrode rotation rate, and the anodic potential limit of the voltammetric scan. The results can be grouped into three distinct types of behaviour defined by the characteristics of the copper sulphide film.

3.1. Type I–Single layer porous Cu_2S film

Type I films were observed at the two lowest [SH⁻] (5.0×10^{-5} M and 1.0×10^{-4} M) irrespective of changes in [Cl⁻] and mass transport conditions. A similar Type-I film was produced at 0.1 M chloride in the [SH⁻] range from 5.0×10^{-5} M to 2.0×10^{-3} M, and also at 0.5 M and 1.0 M chloride providing the [SH⁻] was in the range 5.0×10^{-5} M to 5.0×10^{-4} M, and providing the solution was stagnant or the rotation rate was low (i.e., 10.5 rad/s).

At a stationary electrode, Fig. 1, the shape of the anodic current peak for Cu_2S formation suggests film formation was diffusion controlled. On the reverse cathodic scan, a single, almost symmetrical peak for the reduction of Cu_2S was observed at -1.15 V/SCE. When the electrode was rotated, Fig. 2, the flux of SH^- to the electrode surface was accelerated and the presence of an anodic current plateau, with the current dependent on electrode rotation rate, confirms that film growth was dominantly a diffusion-controlled process. On the reverse scan the anodic current retraced its original path, confirming that film growth was reversible and that the sulphide film did not passivate the Cu surface. The size of the single reduction peak increased with rotation rate, and integration of the anodic and