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Non-uniform film growth and micro/macro-galvanic corrosion of copper in aqueous sulphide solutions containing chloride

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ABSTRACT

The corrosion of copper in aqueous sulphide environments is rapid and can occur under transport limited conditions. At sufficiently high sulphide flux, microgalvanic corrosion can be supported between areas of the surface covered by compact sulphide deposits and other areas covered only by a porous deposit. This leads to excessive crystal growth at the cathodes (compact film) and localized corrosion damage at the anodes (porous film). The transport of Cu(I) between the two areas, required to sustain this process, appears to occur predominantly by the solution transport of Cu-sulphide complex or clusters.

1. Introduction

Precipitation and crystal growth involve a phase transition from a high energy solvated state to a lower energy location in the crystalline phase [1] and can be influenced by features such as the properties of the solvent, the presence of impurities and the substrate grain orientation and, for corrosion processes, the cathodic current density [1–11]. These influences can lead, for corroding systems, to a non-uniform growth of the corrosion film which could influence the distribution of corrosion damage.

In aqueous solutions, sulphide destabilizes Cu at very negative corrosion potentials, leading to its corrosion and the deposition of films on the Cu surface. Previously, we have shown [12–17] that corrosion is rapid, leading to the deposition of chalcocite (Cu_2S), identified by energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). This layer is formed at the Cu_2S/electrolyte interface with the total consumption of sulphide [12]. Under stagnant and controlled convective conditions the morphology of film growth was markedly influenced by transport processes. In a stagnant solution, corrosion was controlled by solution transport, and a non-protective film composed of crystals with a wide distribution of sizes was formed. When the transport process was convectively accelerated, a more coherent and partially protective film with a narrow distribution of crystal sizes was formed. This sensitivity to transport, and the wide distribution in the size of corrosion product crystals when transport is uncontrolled (i.e., under stagnant conditions), suggests local variations in corrosion rate. This raises the spectre that corrosion damage to the Cu substrate will be non-uniform. If this is indeed the case then the commonly adopted specification of a corrosion allowance for nuclear waste containers in lifetime prediction models in Sweden, Finland and Canada [18–20] should be re-examined.

In this paper we describe a series of experiments to determine the details of the corrosion process with a primary emphasis on understanding how the wide distribution in crystal growth rates develops and its role in determining the distribution of damage across the corroded surface. The implications for the corrosion of nuclear waste containers are also addressed. In experiment (i) a Cu specimen was immersed in the solution for 1691 h under natural corrosion conditions. In experiment (ii) half the surface of a Cu specimen was sealed with wax while the other half was exposed to the solution. This partially wax-sealed specimen was then immersed in the solution for 1211 h before the wax was removed and the specimen re-immersed in the same solution for a further 480 h for a total immersion time of 1691 h. In experiment (iii) a Cu specimen was pre-corroded in the solution for 1211 h and then re-immersed galvanically connected to an uncorroded Cu specimen for a further 480 h for a total immersion time of 1691 h.

2. Materials and methods

Experiments were conducted using P-doped (30–100 mg/kg), O-free copper (Cu-OF) provided by the Swedish Nuclear Fuel and Waste Management Co. (SKB), Stockholm. Cu disk working electrodes (1×10^{-2} m in diameter) were cut from plate material. The

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disks were connected to a stainless steel shaft and painted with a non-conductive lacquer to prevent contact of the Cu/steel junction with the solution. The electrodes were then heated (60 °C for 12 h) to promote adhesion of the paint. The exposed flat surface was ground successively with 240, 600, 800, 1000, 1200 grade SiC paper, then polished to a mirror finish using 1 μm, 0.3 μm, and, finally, 0.05 μm Al_2O_3 suspensions. Prior to experiments, electrodes were washed with Type I water (resistivity = 18.2 MΩ·cm (obtained from a Thermo Scientific Barnstead Nanopure 7143 ultrapure water system)), ultrasonically cleaned using methanol (reagent grade), washed with Type I water, and dried using ultra pure Ar.

To ensure anoxic conditions, experiments were performed in an Ar-purged anaerobic chamber (Canadian Vacuum Systems Ltd.), maintained at a positive pressure (2–4 mbar) by an MBraun glove box control system. The oxygen concentration in the chamber was analyzed with an MBraun oxygen probe with a detection limit of 1.4 mg/m^3. The anaerobic chamber was maintained at a total oxygen concentration $\leq$4.2 mg/m^3, which includes the oxygen in both air and vapor. The actual oxygen content of the solution should be less than this value. Even though there is a trace amount of oxygen present, copper sulphide is more stable in sulphide solution than copper oxide based on thermodynamic data (The standard free energy of reaction, $\Delta G^\circ = -101.46$ kJ/mol, for the conversion from Cu_2O to Cu_2S in sulphide solutions at 298 K [21]: $Cu_2O\ (s) + HS^-\ (aq) \rightarrow Cu_2S\ (s) + OH^-\ (aq)$) and available literature [22–25].

The 0.1 mol/L NaCl + x mol/L Na_2S solution ($x = 5 \times 10^{-5}$, 5×10^{-4} and 1×10^{-3} mol/L) was prepared with Type I water, reagent-grade sodium sulphide ($Na_2S{\cdot}9H_2O$, 98.0% assay) and sodium chloride (NaCl, 99.0% assay), to simulate the saline groundwater conditions anticipated in a waste repository.

Electrodes were immersed in the sulphide solutions under natural corrosion conditions (at the corrosion potential, E_{CORR}) for various exposure periods. A standard three-electrode cell with a Pt plate counter electrode and a saturated calomel reference electrode (SCE) was used. Prior to each experiment, electrodes were cathodically cleaned at −1.6 V/SCE for 2 min and then at −1.15 V/SCE for 2 min.

Since exposure periods were long, the $[SH^-]$ was monitored weekly by measuring the pH as described previously [12] and SH^- added to readjust the $[SH^-]$ to its original value. Experiments were performed at 25 ± 2 °C. Corrosion potentials (E_{CORR}) were measured using a Solarton 1287 electrochemical interface and, in galvanically-coupled experiments, the current density was measured using a Keithley 6514 electrometer.

Electrodes removed from solution for surface analyses were rinsed with Type I water for 10 min and dried with cold Ar gas. Analyses were then performed after a minimum period of interim storage (<30 min). The surface and cross-sectional morphologies of corroded specimens were observed using a Leo 1540 scanning electron microscope (SEM) equipped with a focused ion beam (FIB) (Zeiss Nano Technology Systems Division, Germany). The composition of films was qualitatively analyzed by energy dispersive X-ray spectroscopy (EDS) using a Leo 1540 FIB/SEM microscope (the oxygen detection limit is 1 at.%). The Cu content of solutions was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

3. Results and discussion

3.1. The phenomenon of excessive crystal growth

Fig. 1 shows the Cu_2S film formed on Cu after 1691 h of immersion in a 0.1 mol/L NaCl + 5×10^{-4} mol/L Na_2S solution (experiment (i)). Most of the surface is covered with a relatively uniform deposit while some areas have experienced excessive crystal growth as indicated within the oval, Fig. 1(a). Fig. 1(b) shows the film growth kinetics in 0.1 mol/L NaCl solution containing various $[SH^-]$, based on many thickness (d) measurements at various locations in FIB (focused ion beam)-cut cross sections. As shown in Fig. 1a, the film grew non-uniformly leading to the variations in thickness with location. The error bars in Fig. 1b show the standard deviations calculated from this series of measurements. The plotted lines show the linear least squares fits to the data used to obtain the growth laws.

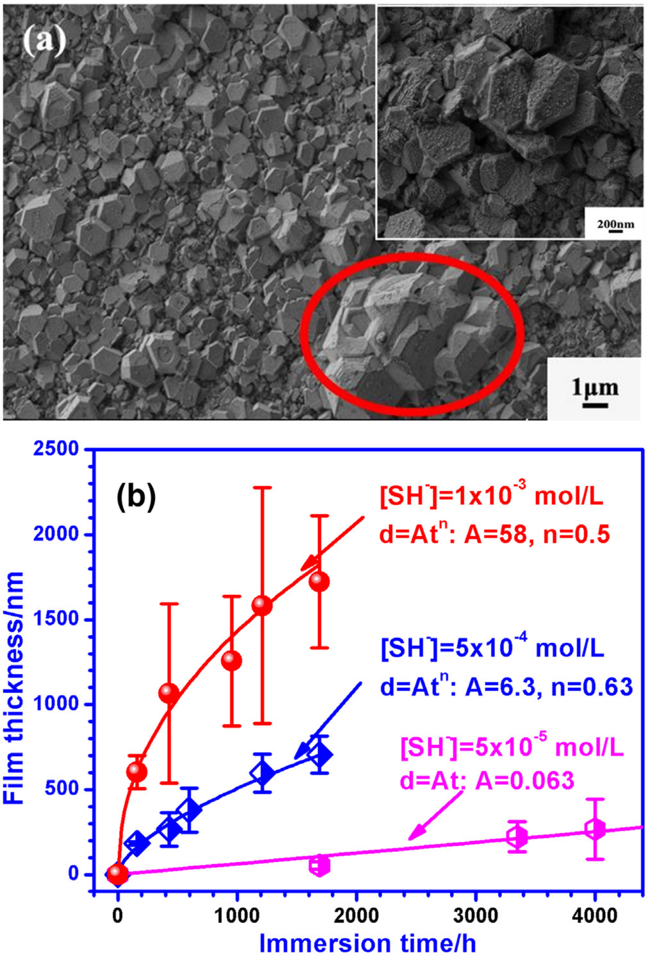

Fig 1. (a) An example of excessive crystal growth on Cu (indicated within the red oval) with an insert showing the surface at high magnification after 1691 h immersion 0.1 mol/L NaCl + 5×10^{-4} mol/L Na_2S solution; and (b) film thickness as a function of immersion time for sulphide films grown in 0.1 mol/L NaCl solutions containing various $[SH^-]$ [12,13,15]. The growth rate laws are indicated for each $[SH^-]$. All of these experiments were performed under natural corrosion conditions. The film growth kinetics in Fig. 1b is cited from Ref. [15]. The linear least squares/linear fit to the experiment data is given as solid line in Fig. 1b, with a fitting dependency of >0.98. The fitting detail have been described in Ref. [12]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

When $[SH^-]$ is low (i.e., 5×10^{-5} mol/L Na_2S), film growth kinetics are linear and, as shown elsewhere [13], the film develops a cellular structure. Impedance measurements showed [13] the rate of interfacial reaction is larger than the diffusive flux of SH^- to the corroding surface, and Cu_2S growth is controlled primarily by SH^- diffusion in solution consistent with the linear growth of a non-protective film. However, when $[SH^-]$ is high (1×10^{-3} mol/L), the film deposits with a well defined crystal structure, and the growth kinetics are parabolic indicating the diffusive flux is greater than the interfacial reaction rate leading to film growth controlled by Cu^+ diffusion in the now protective film. In addition, as $[SH^-]$ increases,

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