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Effect of temperature on copper corrosion in high-level nuclear waste environment

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Abstract: The effect of temperature on the corrosion behavior of copper in simulated high-level nuclear waste environment was systematically studied. Electrochemical methods, including electrochemical impendence spectra, Mott–Schottky technology, cyclic polarization, and potentiostatic polarization, were employed to characterize the corrosion behavior of copper at different temperatures. Stereoscopic microscopy and scanning electron microscopy were used to examine the surface morphology, and X-ray photoelectron spectroscopy analysis was used to identify the composition of the passive film. The experimental results show that corrosion resistance of the passive film does not blindly decrease with the increase of temperature but increases at 60 °C owing to a compact outer layer; there is a potential for pitting corrosion, which decreases as the temperature increases. The main product of copper in an anaerobic aqueous sulfide solution is Cu_2S but the content of CuS increases at higher temperatures. The whole passivation range shows p-type semiconductor characteristics and the magnitude of the acceptor density is 10^{23} cm^{-3}, which increases with increasing temperature.

Key words: copper corrosion; sulfide; nuclear waste disposal; temperature; electrochemical performance

1 Introduction

A proposed method for the disposal of Swedish, Finnish, or Canadian high-level nuclear waste is to place it in corrosion resistant containers and bury it 500−1000 m deep in a granitic repository [1−4]. These containers would be fabricated with an inner layer of cast iron and an outer shell of oxygen-free copper (30−50 mm in thickness). Although Cu was chosen for its thermodynamic resistance to corrosion in anoxic environments, the long-term corrosion behavior of copper in contact with sulfide-containing, saline, anoxic environments is far from being well-understood. So, a fundamental understanding of the passive state on this metal in relevant environments is urgently required. The most likely corrosive agent in the groundwater to which the containers will be exposed is sulfide, derived from either mineral dissolution (i.e., pyrite, FeS_2) or microbial production from sulfates (i.e., via reaction of sulfate-reducing bacteria) [5,6]. In ground water anticipated in a geologic repository, the sulfide and chloride concentrations will be in the range of 10^{-7}−10^{-4} mol/L and 0.1−1.4 mol/L, respectively [7].

CHEN et al [8−10] studied the kinetics of corrosion film growth and long-term corrosion of copper in chloride solution containing sulfide at room temperature. Kinetic studies revealed that two types of growth processes are dependent on $[SH^-]$. At relatively high concentrations ($[SH^-]=5.0\times10^{-4}$ mol/L), film growth follows a parabolic law and is governed by the transport of Cu^+ ions through the Cu_2S matrix or along grain boundaries in the Cu_2S film. However, when $[SH^-]$ is lower ($[SH^-]=5.0\times10^{-5}$ mol/L), film growth is controlled by SH^- diffusion and the kinetics follow a linear growth law, leading to a porous non-protective film. MARTINO and PARTOVI [11] focused on a wide range of sulfide and chloride concentrations using rotating disk electrodes at room temperature. These studies show that three distinct types of films are formed depending on the sulfide concentration, flux of sulfide to the electrode surface, and chloride concentration of the solution.

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Further, the film properties and the growth mechanism were determined by the competition between sulfide diffusion in solution and the rate of interfacial reactions on the copper surface.

It is obvious that most of the above studies focused on comparison of the materials performance at room temperature and relatively few studies on the effect of temperature on the corrosion behavior of copper in ground water environments. However, the canister material might experience a wide range of temperatures in a high-level nuclear waste repository depending on the location; time and temperature definitely have a great influence on the corrosion of copper canisters, which changes the service life of the copper canister. The canisters will experience different environmental scenarios (initially oxic, but then anoxic) and an increase in temperature up to 90 °C in around 10 years, and then a decrease to 30 °C after closure for 2000 years [7]. Therefore, it is the main objective of this study to systematically study the effect of temperature on the corrosion behavior of copper in the repository environment.

2 Experimental

2.1 Materials and electrode preparation

All experiments were performed with phosphorous-doped, oxygen-free copper (Cu-OF) with a purity of 99.999%. Working electrodes were prepared using copper billets of 1 cm × 1 cm and threading them into thin copper rods. Electrodes were then encased in polytetrafluoroethylene (PTFE) holders using epoxy resin to prevent any contact of the aqueous environment with the copper rod. All samples were ground with SiC paper up to 2000 grit and to a mirror finish using 1 μm Al_2SiO_5 suspensions, and then washed with deionized millipore water (18.2 MΩ·m), ultrasonically cleaned in ethanol and deionized water for 20 min, and dried with cool air prior to the experiments.

2.2 Solutions

All solutions were prepared using deionized millipore water (18.2 MΩ·m). Solutions contained 2×10^{-4} mol/L reagent-grade sodium sulfide ($Na_2S\cdot9H_2O$, 98.0%) and 0.1 mol/L sodium chloride (analytical grade NaCl, 99.0%) to simulate the disposal repository underground environment. A solution with a pH of 9.0 was established with 0.2 mol/L borate buffer solution. To avoid contamination from atmospheric O_2, all experiments were performed in an anoxic chamber in N_2-purged solutions, and electrodes were cathodically cleaned at −1.3 V (vs SCE) for 60 s prior to the experiments.

2.3 Electrochemical cell and equipment

The electrochemical measurements were performed in a conventional three-electrode cell. A saturated calomel electrode (SCE) and Pt plate were employed as reference electrode (RE) and counter electrode (CE), respectively. The reference electrode was connected to the cell through an electrolyte bridge/Luggin capillary. Electrochemical impedance spectroscopy (EIS) with a frequency range from 100 kHz to 10 mHz and potentiodynamic polarization curves with a scanning rate of 0.1667 mV/s were obtained using a PARSTAT 2273 workstation. While investigating the influence of temperature, we used a water bath to stabilize the temperature of the electrochemical cell.

2.4 Morphology observation and composition analysis

The surface of the samples was observed using a scanning electron microscope (SEM) (Quanta 250) and the chemical composition of the surface films formed was investigated by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250xi, Thermo Fisher) on an instrument equipped with an Al K_α X-ray source ($h\nu$= 1486.6 eV) operated at 150 W. Because of the possible oxidation of the electrodes in air, they were sputter-coated with a 5 nm passive film using a 3 kV, 1 μA Ar^+ ion beam. The charge shift of the spectra was corrected by assuming that the C 1s peak was at 284.8 eV; curve fitting was performed with commercial software XPS peak version 4.1 using Shirley background subtraction and a Gaussian–Lorentzian tail function.

3 Results and discussion

3.1 Electrochemical impedance spectroscopy

EIS is an efficient method to study surface conditions of metals, and is also a powerful tool for evaluating the protectiveness of a corrosion product layer formed on metals [12,13]. Figure 1 shows Nyquist and Bode plots recorded on oxygen-free copper in anoxic 2×10^{-4} mol/L $Na_2S\cdot9H_2O$ and 0.1 mol/L NaCl solution after 2 h immersion at various temperatures. The spectra recorded in the two different frequency sweep directions (high-to-low and low-to-high) curves in the Nyquist and Bode plots are almost the same, which implies that steady state conditions were largely achieved. We can clearly see that the corrosion resistance did not decrease blindly with increasing temperature. There was a rise while the temperature reached 60 °C and the impedance of the sample at 60 °C was larger than that at either 50 °C or 70 °C, which simply indicates that the protectiveness of the corrosion products at this temperature was much better. There is an evidence that the sulfide film forms as two distinct layers: an inner layer (IL) that is thin and coherent and an outer layer (OL) that is composed of deposited products [8,11].