Passivity Breakdown on Copper: Influence of Chloride Ion

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ABSTRACT

Passivity breakdown and pitting on pure copper, the assumed material for the outer canisters for the isolation of high-level nuclear waste in Sweden and Finland, has been studied in simulated, sulfide- and chloride-containing granitic rock groundwater and the data are interpreted in terms of the Point Defect Model (PDM). The near normal distribution in the critical breakdown potential (V_c) measured in deaerated sodium sulfide solutions with different chloride concentrations and for variable pH (= 8-10) is in satisfactory agreement with the quantitative prediction of the PDM. The critical areal concentration of condensed cation vacancies at the metal/film interface that leads to passivity breakdown, as predicted by the PDM from the experimental dependence of the V_c on the square root of the voltage sweep rate, $\xi < 1.09 \times 10^{15} \text{ cm}^{-2}$, is in excellent agreement with that calculated from the unit cell dimensions of the substrate Cu ($\xi \approx 1.53 \times 10^{15} \text{ cm}^{-2}$) and the barrier layer sulfide (Cu_2S) ($\xi \approx 7.66 \times 10^{14} \text{ cm}^{-2}$) for vacancy condensation upon the metal lattice or upon the cation sublattice of the film, respectively. This observation provides convincing evidence for the validity of the PDM for modeling passivity breakdown on Cu sulfide- and chloride-containing granitic rock groundwater.

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1. Introduction

Sweden's KBS-3 multi-barrier plan for the disposal of high-level nuclear waste (HLNW) is partly predicated on the assumption that copper, the material from which the canisters will be fabricated, is a semi-noble metal when in contact with water. The environment within the proposed repositories is not pristine, pure water, but instead is brine containing a variety of species, including halide ions, sulfur-containing species, as well as iron oxidation products. Recognizing that copper metal loses much of its corrosion resistance in the presence of sulfide ion and other sulfur-containing species [1–6], with the metal forming a Cu_2S barrier layer of the passive film, Sharifiasl and Macdonald expanded the Point Defect Model (PDM) [7,8] representation of a passive film to cover of the formation of Cu_2S barrier layer, which has been described in detail elsewhere [1]. Study of the relationships that exist between the concentrations of aggressive ions and species that determine the identity of the barrier layer (HS^-, S^{2-}) and that result in passivity breakdown (Cl^-) and the critical breakdown potential (V_c) for localized corrosion processes, such as pitting corrosion, is expected to indicate whether localized corrosion damage (LCD) is likely to develop on the copper canisters in the repository. The initial events in the accumulation of LCD are passivity breakdown and pit nucleation. The PDM provides a deterministic description of passivity breakdown on metals and alloys [8–14] and hence provides a suitable basis for eventually predicting whether localized corrosion damage will occur in the operating repository. The purpose of the present study of passivity breakdown on copper is to assess the ability PDM for quantitatively describing passivity breakdown in the presence of chloride ion and sulfide ion.

2. Passivity breakdown

The influence of dissolved sulfide species on the electrochemical behavior of copper and its alloys is complex and no completely satisfactory mechanism has yet been reported. Several studies of copper corrosion in a sulfide-polluted environment have revealed that copper forms a bilayer corrosion product comprising an inner Cu_2S "barrier" layer and a thicker CuS outer layer [15–17]. Chialvo and Ariva [15] proposed that reaction of copper in alkaline sodium sulfide solutions undergoes the following path: Cu/electrolyte → Cu/$Cu_{1.8}S$/electrolyte → Cu/$Cu_{1.8}S$/Cu_2S/electrolyte → Cu/$Cu_{1.8}S$/Cu_2S/CuS/electrolyte; that is, they postulate the formation of a tri-layer passive film. They

concluded that cupreous sulfide (Cu_2S) is predominantly formed at potentials lower than -0.6 V vs. SHE, while cupric sulfide (CuS) forms after long electrolysis at higher potentials. The work of Macdonald et al. [18] suggested the formation of a duplex sulfide film on Cu-Ni alloys in deaerated sea water containing sulfide species. Syrett [19], on the other hand, reported that the bilayer film comprises an oxide barrier (inner) layer and a Cu_2S (or $Cu_{2-x}S$) outer layer. This oxide/sulfide bilayer structure is likely to be seen in a repository only while significant oxygen is present in the environment; that is during the initial "oxic" period. Once the initially trapped oxygen has been consumed during this initial oxic period (a few decades), and the system becomes more reducing in nature (during the much longer anoxic period) the formation of an oxide barrier layer is judged to be unlikely. Thus, based on the thermodynamic information of the system, Macdonald et al. [20] postulated that the presence of sulfide species in a sea water solution will shift the corrosion potential to more active values that could satisfy the thermodynamic criterion for spontaneous formation of cuprous sulfide with hydrogen evolution acting as the principal cathodic partial reaction.

The "activating" role of sulfide ion on the corrosion of copper is, perhaps, best illustrated by the Corrosion Domain Diagrams for copper in the absence [Fig. 1(a)] and in the presence [Fig. 1(b)] of sulfide. In these figures, the quantity P is defined as $P = f_{H_2}^{1/2} a_{Cu^+}$ and $P = \frac{f_{H_2}}{a_{HS^-}}$, respectively, corresponding to the corrosion reactions: $Cu + H^+ \rightarrow Cu^+ + 1/2 H_2$ and $2Cu + HS^- + H^+ \rightarrow Cu_2S + H_2$ The quantity, P^e, corresponds to the value of the partial reaction quotient, P, at equilibrium. The diagrams plot P vs pH and are divided into two regions: for $P > P^e$, copper is thermodynamically immune and corrosion cannot occur, whereas if $P < P^e$ corrosion is spontaneous. Thus, if P is initially below the equilibrium line, in a closed system, corrosion will occur and corrosion products (Cu^+, H_2) will accumulate adjacent to the metal surface, resulting in an increase in the value of P. After a sufficiently long time, $P = P^e$ for the prevailing temperature and further corrosion becomes limited by the rate of mass transport of the corrosion products away from the copper interface. The principal role of bisulfide ion (and many other polysulfide species (e.g., HS_x^-) is that the value of P^e shifts by 20 orders of magnitude in the positive direction making the immune state impossible to achieve practically. CDDs were originally derived by one of the present authors [21] to resolve a controversy raging in Sweden over the report by Hultqvist, et al. [22–24] that copper corrodes in deaerated pure water as determined by the evolution of hydrogen, whereas copper had always been considered to be immune under these conditions and hence its classification as being a "semi-noble" metal. With reference to Fig. 1(a) any combination of hydrogen fugacity (pressure) and cuprous ion activity for which $P > P^e$ suffices to render the copper immune and likewise any combination of these variables for which $P < P^e$ suffices to render corrosion spontaneous. In the absence of exact values for the hydrogen fugacity (pressure) and cuprous ion activity in the experiments of Hultqvist et al. [22–24] and those of their detractors, it is suggested that the relative values of P and P^e provide a thermodynamically-viable resolution of the controversy.

Recently, several studies on the corrosion and electrochemistry of copper in sulfide-containing environments have been published [5,25–30]. These studies were performed in sodium chloride solutions containing different concentrations of sulfide species that are expected to be present in the repository in Sweden. Chen et al. [25] studied the kinetics of the copper corrosion in a neutral sodium chloride solution containing a small concentration of sulfide ion as a function of time under open circuit potential conditions. Their results revealed that, while chloride ions can influence the morphology of the copper sulfide deposits, there is no evidence of its direct role in the copper dissolution reaction. Combined electrochemical and morphological studies in their work have shown that the corrosion film formed on the copper surface comprised a single layer of Cu_2S, with the thickness increasing with immersion time [25]. Mott-Schottky analysis by Yunhan et al. [31] indicate that a bi-layer sulfide film forms, comprising a p-type barrier layer of Cu_2S and probably an outer layer of CuS, which is n-type in electronic character. The outer layer was not observed to form at 25 °C and at 50 °C, but was observed to form intermittently at 75 °C. Given this, we replace, in the Point Defect Model (PDM), the usual oxide barrier layer of a metal-H_2O system with the metal sulfide (Cu_2S) in formulating of physico-electrochemical description of the passive state on copper in sulfide-containing, aqueous media.

The PDM [7–14] proposes that cation vacancies ($V_M^{\chi'}$) generated at the film/solution interface move to the metal/film interface, and are annihilated by cation injection into the film from the metal.

$$m + V_M^{\chi'} \rightarrow M_M + \upsilon_m + \chi e' \qquad (1)$$

where m and υ_m are a metal atom and a metal vacancy in the metal phase, respectively; and $V_M^{\chi'}$ and M_M are a cation vacancy and a cation in normal cation sites on the cation sublattice of the barrier layer. The annihilation rate of the cation vacancies ($V_M^{\chi'}$) at the metal/film interface due to Reaction (1) is designated as J_m. Aggressive anion absorption (e.g. chloride anion) into surface sulfur vacancies $V_S^{\bullet\bullet}$ is postulated to catalyze the generation of cation vacancies possibly via a Schottky pair reaction [$Null \leftrightarrow V_M^{\chi'} + \frac{\chi}{2} V_S^{\bullet\bullet}$] or anion-assisted cation extraction (ion desorption/vacancy pair generation). Both processes are autocatalytic in the sulfur vacancy, in that the sulfur vacancies are regenerated at the periphery of the vacancy condensate and hence are available to absorb additional aggressive anion. The increased concentration of cation vacancies in the film at the film/solution interface (f/si) leads to an enhanced flux of the cation vacancies (J_{ca}) towards the metal/film interface (m/fi) [7–14]. If the cation vacancies ($V_M^{\chi'}$) cannot be totally annihilated at the m/fi by Reaction (1), or if the vacancies on the metal lattice (υ_m) on the metal side of the m/fi cannot be annihilated by process such as dislocation climb or by diffusion into the bulk metal, the excess vacancies arriving at the m/fi ($J_{ca} > J_m$) condense on the respective lattices. This process will continue until the areal vacancy concentration in the condensate exceeds a critical value (ξ), resulting in local separation of the barrier layer from the substrate metal. This local vacancy condensation/separation process continues at the periphery of the condensate causing the condensate to expand and preventing the film from penetrating into the substrate via the generation of sulfur vacancies via the reaction

$$m \rightarrow M_M + \frac{\chi}{2} V_S^{\bullet\bullet} + \chi e' \qquad (2)$$

However, dissolution continues at the f/si with the result that the barrier layer over the condensate thins at a rate that is determined by the dissolution rate and, at some point, the "cap" (remnants of the barrier layer) over the condensate ruptures to mark a passivity breakdown event [7–14]. The critical areal concentration (#/cm^2) of cation vacancies that must condense (ξ) for separation to occur between the barrier layer and the metal substrate is determined by the structures of the metal and the barrier layer, depending on whether condensation is envisioned to occur on the metal lattice or on the cation sublattice of the film. According to this mechanism, taking into account only chloride anion adsorption/Schottky-pair vacancy generation, the following relationship for the critical breakdown potential (V_c) was derived [6–9].

$$V_C = \frac{4.606 RT}{\chi \alpha F} \log\left(\frac{b}{D}\right) - \frac{2.303 RT}{\alpha F} \log(a_{Cl^-}) \qquad (3)$$