The Point Defect Model for the Passive Sulfide films on Copper

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Sweden’s KBS-3 plan for the disposal of high level nuclear waste (HLNW) is partly predicated upon the assumption that copper, the material from which the canisters will be fabricated, is thermodynamically immune to corrosion when in contact with pure water under anoxic conditions. In other words, copper was classified as being a noble metal like gold. In the immune state, corrosion cannot occur, because any oxidation process of the copper is characterized by a positive change in the Gibbs energy, rather than a negative change demanded by the Second Law of Thermodynamics for a spontaneous process. [1] Despite this argument, copper and its alloys may subject to the corrosion in different situations for example, in aerated chloride medium, the corrosion of copper takes place at noticeable rate. [2]

In this work the passivity of copper in deaerated aqueous 0.1 M NaCl + X M Na₂S₉H₂O with X being equal to 2×10⁻⁴ M, 4×10⁻⁴ M and 2×10⁻³ M as a function of applied potential and temperature were explored by means of potentiodynamic polarization and electrochemical impedance spectroscopy. The electronic and compositional properties of the passive layer were investigated with Mott-Schottky analysis and X-ray photoelectron spectroscopy XPS. A point defect model (PDM) for formation and dissolution of passive sulfide film on copper is proposed. Finally, the behavior of the system interpreted in terms of reaction mechanisms and kinetic parameters extracted from the experimental impedance data by mathematical optimization. It is found that metal vacancies are predominant defect in the film which is in agreement with p-type character of the film.

References