Mechanistic Model for the Passive Dissolution of Ni-Cr-Mo Alloys

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In this paper, a mechanistic model for the passive dissolution of Ni-Cr-Mo alloys at low temperatures, based on the Point Defect Model (1), is proposed. The model is applied to the description of passive behavior of Alloy 22 (Ni-22Cr-13Mo-3W-3Fe). Fundamental charge transfer reactions at the metal-film and film-solution interfaces used to study binary alloys (2) were extended to ternary systems, including reactions for the injection of interstitial species into the oxide lattice at the metal-film interface. The passive dissolution of Ni-Cr-Mo alloys is controlled by the formation of a bilayered oxide film on the metal surface. The inner oxide film is chromium-rich and the outer layer oxide is nickel- and molybdenum-rich. We assumed that the inner oxide is the film that regulates the passive behavior and that it contains chromium and molybdenum as interstitial defects, nickel as a substitutional and interstitial defect, and oxygen and chromium vacancies. Thermodynamic and kinetic arguments are provided to support the notion that the predominant conduction mode through the oxide film in Ni-Cr-Mo alloys is interstitial conduction. According to the Point Defect Model, the injection of interstitial ions from the alloy into the oxide lattice is accompanied by the creation of vacancies in the alloy at the metal-film interface.

An analytical expression was derived for the passive current density. This expression is consistent with experimental results indicating that the passive current density for Alloy 22 is essentially independent of the applied potential up to the potential for transpassive dissolution, and also independent of environmental conditions such as pH and chloride concentration (3, 4). Diffusion of vacancies in the alloy was described using the following constitutive equation

$$J_A = -\frac{D_A}{c_v^o}\left(c_v \nabla c_A - c_A \nabla c_v\right) = -J_v \qquad [1]$$

where J_A is the flux of element A (Ni, Cr, or Mo); J_v, the vacancy flux; D_A, the solid-state diffusion coefficient; c_v, the vacancy concentration; c_v^o, the vacancy equilibrium concentration at a reference temperature, and c_A, the atomic concentration. We assumed that the rate of ejection of interstitial ions from the alloy is proportional to their atomic fractions at the metal-film interface, and that the solid state diffusion coefficients for the three alloying elements are similar. From finite-difference computations we derived an anodic passive current density that decreases as a function of time due to the accumulation of vacancies at the metal-film interface. Details on the mathematical approach are available elsewhere (5). Accumulation of these vacancies could potentially render the oxide-film unstable over extended periods. Other authors have recognized this problem for high-temperature systems (6). We concluded that the dissolution process could be initially non-stoichiometric, but it evolves toward stoichiometry in the long-term. This numerical conclusion is in agreement with experimental

observations reported elsewhere (7, 8). This conclusion depends on the assumption of the similitude of the diffusion coefficients for the alloying elements, but it is independent of the assumed values of the rate constants of the fundamental charge transfer reactions.

We verified with potentiostatic experiments that there is an exponential dependence between the inverse of the temperature and the passive current density in the range from 25 to 95 °C [77 to 203 °F]. The derived activation energy is approximately 45 kJ/mol [10.7 kcal/mol]. This activation energy can be attributed to an Arrhenius dependence on the temperature of the rate constants for the rate of injection of interstitials into the oxide lattice.

The analysis in this paper provides insights on whether Alloy 22 is a long-lasting material, in the absence of environmental and electrochemical conditions leading to localized corrosion or stress corrosion cracking. Alloy 22 is the proposed material to construct containers to enclose radioactive waste to be disposed in the proposed geologic repository at Yucca Mountain, Nevada, U.S.A. Although the oxide film could become unstable because of the presence of vacancies, the finite difference computations indicate that there could be enrichment of chromium at the metal-film interface, facilitating the reformation of a protective oxide film in case of spalling. Also, the rate of vacancy accumulation significantly decreases with decreasing temperatures.

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