

Corrosion Behavior of Titanium Grade 7 in Fluoride-Containing NaCl Brines

Tiangan Lian, Michael T. Whalen, Lana Wong
Lawrence Livermore National Laboratory
7000 East Ave, L-631,
Livermore, CA 94550

Titanium Grade 7 (UNS R52400) is a titanium-based alloy with 0.12-0.25% Pd. The addition of the small amount of palladium is to ennoble the corrosion potential of Ti, thus improving the corrosion resistance of titanium in reducing environments. In most aqueous environments, Ti and Ti alloys demonstrate an excellent corrosion resistance due to the protective oxide films spontaneously formed and remain stable on the surface. However, Ti and Ti alloys are susceptible to corrosion in fluoride-containing environments due to the formation of complexes such as TiF_6^{2-} and TiF_6^{3-} , which are stable and soluble in electrolyte solutions. Without the presence of fluoride, only slight effects from $[Cl^-]$, pH and temperature have been reported [1]. It has been reported that the kinetics of passive corrosion of titanium in neutral solutions are controlled by the migration of the defects in the oxide across the surface film [2]. Thus, the increase in thickness and improvement in film properties, by thermal oxidation, would lead to a significant decrease in the susceptibility of film breakdown and the passive corrosion rate.

This report summarizes recent experiment results in studies of the environmental influence on the corrosion behavior of Titanium Grade 7 (Ti-7) in NaCl brines containing fluoride. The environmental factors to be studied include temperature, pH, chloride and fluoride concentration. This report also includes the effects of oxide film, formed during an anneal treatment, on the corrosion behavior of Ti-7. Polarization measurement techniques including potentiodynamic and potentiostatic scans were used to characterize corrosion kinetics and susceptibility. Due to unique alloying system in Titanium Grade 7, the long-term corrosion behavior is heavily influenced by the surface enrichment of Pd. Use of electrochemical impedance spectroscopy in conjunction with a potentiostatic scan will reveal the transformation in the corrosion behavior as function of Pd enrichment on the metal surface. Surface characterization was done using various analytical techniques including X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM).

The effect of fluoride ion on the corrosion behavior of Ti-7 is strongly dependent on the solution pH. In neutral (pH 8) and alkaline (pH 11) solution, fluoride ion did not affect the corrosion rate significantly, even though it altered anodic polarization curve drastically (Figure 1). With pH decreased to 4, the corrosion rate of Ti-7 was increased significantly by the presence of fluoride (Figure 2).

Acknowledgements:

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No W-7405-Eng-48. This work was supported by the Yucca Mountain Project, which is part

of the DOE office of Civilian Radioactive Waste Management.

References:

1. C. S. Brossia and G. A. Cragolino, CORROSION, Vol. 57, No. 9. pp.768-776, 2001.
2. T. Hurlen and S. Hjornkol, Anodic growth of passive films on titanium, Electrochimica Acta, 36, pp. 189-195, 1991

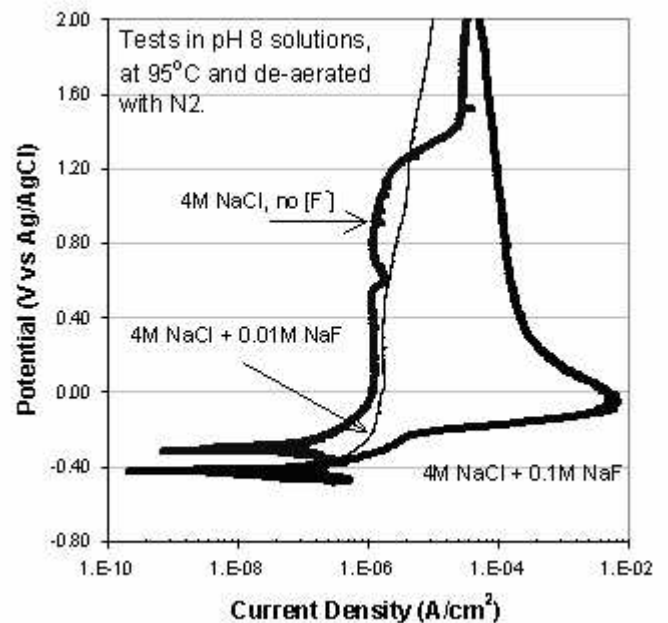


Figure 1. Fluoride Effects at pH 8 on Anodic Polarization Behavior of Titanium Grade 7 in 4 mol/L NaCl Solutions, at 95°C and de-aerated with N_2

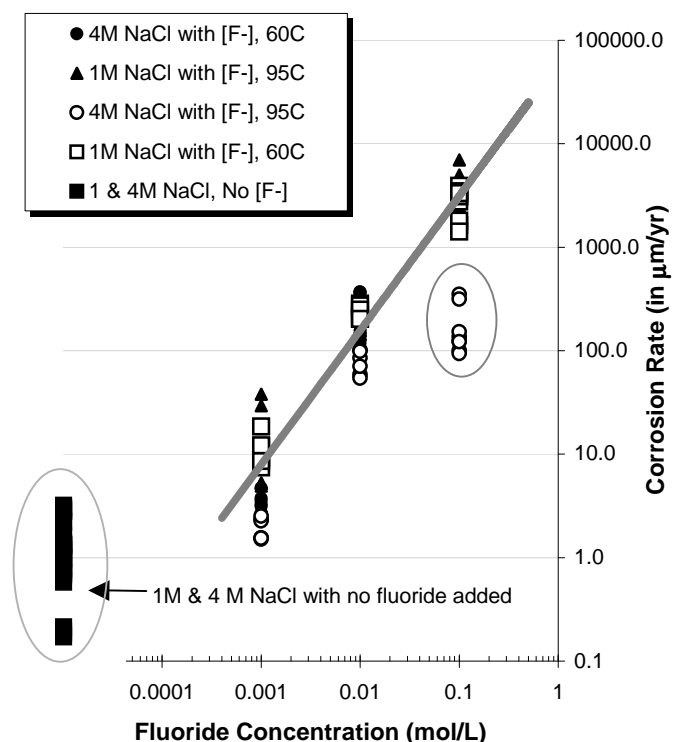


Figure 2. Corrosion rate of Titanium grade 7 in acidic (pH 4) NaCl solutions as a function of fluoride concentration