

Oxide Film Formation on Alloy 600 as a Function of Potential

D. Mizzi¹, A.Y. Musa¹, S. Ramamurthy², J.C. Wren¹
¹Department of Chemistry, ²Surface Science Western
 the University of Western Ontario,
 London, Ontario, Canada, N6A 5B7

Inconel® alloy 600 is a nickel-based alloy with a composition of 15% Cr, 8% Fe, 1% Mn and balance Ni. Due to its high resistance to corrosion, alloy 600 is frequently used for thin-walled heat exchanger tubing, particularly in the steam generators in nuclear power plant.

The effects of pH (8.4 and 10.6), temperature (25 °C and 80 °C) and γ -radiation on the corrosion of alloy 600 in a deaerated 0.01 M borate solution was studied by analyzing the oxide formed on the alloy surface. Electrochemical techniques (such as cyclic voltammetry and EIS (electrochemical impedance spectroscopy)) combined with ex-situ surface analyses such as Auger electron spectroscopy) were used.

The results show the existence of three characteristic potential regions of oxide formation. These regions are consistent with the stabilities of oxides as determined by redox equilibrium potentials (Figure 1).

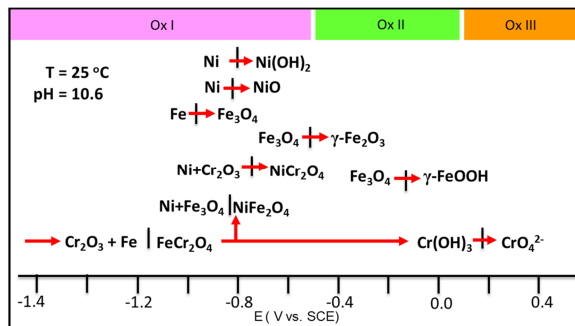


Figure 1: Calculated equilibrium potentials for the redox reactions relevant to the oxidation of alloy 600 at pH 10.6.

In region Ox I ($E < -0.7 V_{SCE}$ at pH 10.6), oxide formation is limited to the conversion of the pre-existing air-formed Cr_2O_3 layer on alloy 600 to a $FeCr_2O_4$ -like layer. The oxidation of Fe^0 to Fe_3O_4 is also possible, but cannot compete with the rate of Fe oxidation to form the more stable $FeCr_2O_4$ until the chromite layer is saturated with Fe^{II} . Consequently, EIS and AES analyses of the oxide films grown at potentials in Ox I for 36 h showed a single layer structure consisting mainly of $FeCr_2O_4$.

In Ox II ($-0.7 V_{SCE} < E < 0.1 V_{SCE}$), the oxidation of Fe^0 to form Fe_3O_4 on the chromite layer can occur at a reasonable rate, and the oxidation of Ni^0 to Ni^{II} to form $NiFe_2O_4$ is thermodynamically possible. Ni^{II} may also form NiO or $Ni(OH)_2$ or be incorporated into the chromium oxide layer to form a $NiCr_2O_4$ -like oxide is thermodynamically possible, but this kinetically prohibited. At the lower end of Ox II the oxidation is limited to the formation of magnetite on the chromite layer. At the higher end of this potential region, the formation of $NiFe_2O_4$ can occur on the $FeCr_2O_4$ layer. The EIS analyses of the films grown at potentials in this region show the presence of such a two-layer structure.

In Ox III ($E > 0.1 V_{SCE}$), oxidative dissolution of Cr^{III} to soluble Cr^{VI} is possible. This leads to the loss of passivation by the destruction of the chromium containing oxide layer. The films grown in this region have a single-layer structure composed mainly of Ni and Fe mixed oxide.

Change in pH did not affect the oxide film formation; the absolute values of all of the redox equilibrium potentials shifts equally by 59 mV per unit pH change. Changing temperature also had no significant effect on the characteristic oxidation potential regions and the oxide formation mechanisms. However, γ -irradiation was found to significantly increase the corrosion potential on alloy 600 (Figure 2). This does alter the oxide formation. In this presentation, the mechanisms whereby pH, temperature and γ -irradiation influence the rates of different reaction paths to form oxides will be discussed.

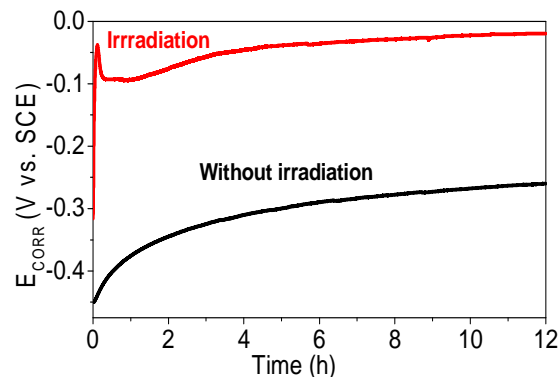


Figure 2: E_{CORR} as a function of time for alloy 600 in a deaerated pH 10.6, 0.01 M borate solution at 25 °C.