Analysis of the Passivation and Local Dissolution of Ni-Cr-based Alloys using the Cabrera-Mott and Point Defect Models

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ABSTRACT

In Fe-Cr based steels, the effects of low concentrations of alloying elements such as N, Mo, and W are somewhat understood with respect to corrosion and passivation. Such alloying often achieves significant improvements in corrosion resistance [1]. However, the roles of alloying elements in a Ni-Cr system are much less well understood. Upon adding small to intermediate concentrations of Mo to Ni-Cr, the corrosion resistance improves dramatically [2]. The Pitting Resistance Equivalent Number can forecast corrosion resistance based on major and minor alloying element concentrations but is empirical and does not provide predictive capabilities nor scientific insights [4]. The goal of this study is to identify the mechanism(s) by which alloying elements improve aqueous passivation in the Ni-Cr-Mo system at the atomic scale and to investigate the oxide properties of the protective passive film. The alloys under study are Ni-11Cr, Ni-11Cr-6Mo, Ni-22Cr, Ni-22Cr-6Mo, and Ni-22Cr-6Mo-3W, wt%, polycrystalline solid solutions.

Previous studies have postulated the influence of different elements on passivity in acidic and high [Cl⁻] environments [3,5]. Cr has been shown to provide passivity during repassivation and enhance resistance to corrosion in oxidizing acids while Mo enables repassivation during oxide film breakdown and increases the resistance to reducing acids [3]. Electrochemical impedance spectroscopy (EIS) studies have been used to analyze the passive film for a Ni-22Cr-13Mo-3W-3Fe-2.5Co, wt%, alloy in varying environments [4].

This presentation explores DC and AC electrochemical techniques for exploring controlled growth of passive oxide films on Ni-Cr alloys. Potentiostatic and galvanostatic holds were used in aqueous chloride and chloride-free solutions of increasing acidity. The data was analyzed using the Cabrera-Mott (C-M) and Point Defect (PDM) models in order to investigate their applicability to the case of Ni-Cr oxide growth with varying concentrations of minor alloying elements [6,7].

A major challenge to the application of either C-M or PDM is that the film thickening rate must be assessed independently from the total oxidation rate. Inductively Coupled Plasma-Optical Emission Spectroscopy indicates that a significant portion of the applied anodic charge during oxidation is associated with direct cation ejection and/or dissolution of the oxide into solution rather than thickening of the film. Therefore, the oxide growth rate and charge must be extracted from the total current for C-M and PDM analysis.

EIS techniques were used to characterize and model the electrochemically grown oxides, represented as a constant phase element, to enable the calculation of oxide thickness. The impedance data following potentiostatic oxide growth was compared to the data produced from single frequency EIS where the impedance was continuously recorded in order to extract the variation of oxide charge and thickness over time. The oxide thicknesses calculated using these methods was related to the charge that goes toward oxide film growth. By comparing these values to the potentiostatic or galvanostatic total charge, the portion involved in dissolution was removed for C-M and PDM analysis. Subsequently, diagnostics were used to test the applicability of C-M and PDM models. Results are reported herein.

Ex situ Raman and X-ray Photoelectron Spectroscopy were utilized to characterize the chemical and molecular identities of the oxide film, accurately calculate the thickness, and test the accuracy of the EIS-dependent oxide calculations. These *ex situ* methods corroborated the determination of the potentiostatic and galvanostatic charges associated with the growth of the oxide.

REFERENCES
[1] Sedriks, A.J. (1996). *Corrosion of stainless steels* (2nd ed.). New York: Wiley
[2] Bocher, F., Huang, R., & Scully, J. R. (2010). Prediction of critical crevice potentials for Ni-Cr-Mo alloys in simulated crevice solutions as a function of molybdenum content. *Corrosion*, 66(*5*).
[3] Lloyd, A. C.; Noel, J. J.; McIntyre, S.; & Shoesmith, D. W. (2004). Cr, Mo, and W alloying additions in Ni and their effect on passivity. *Electrochimica Acta*, 49, 3015-3027.
[4] Combrade, P. (2001). C*orrosion mechanisms in theory and practice* (2nd ed.). CRC Press: Marcus. 349-397.
[5] Jakupi, P.; Zagidulin, D.; Noel, J.J.; & Shoesmith, D.W. (2011). The impedance properties of the oxide film on the Ni-Cr-Mo Alloy-22 in neutral concentrated sodium chloride solution. *Electrochimica Acta*, 56, 6251-6259.
[6] Davenport, A.J. & Lee, B. K. (2012). Passive film growth kinetics for iron and stainless steel, *Electrochemical Society Proceedings*, 13, 187-197.
[7] Marshall, P. I. & Burstein, G. T. (1984). Effects of alloyed molybdenum on the kinetics of repassivation on austenitic stainless steels, *Corrosion Science*, 24(*5*), 463-478.