

## Connection Between Atomic Scale Characterization and Electrochemical Behavior During Passivation of Single Crystals on Ni-Cr and Ni-Cr-Mo Alloys

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### ABSTRACT

Ni-Cr and Ni-Cr-Mo alloys owe their outstanding corrosion resistance to the surface enrichment of passivating Cr(III) oxides and synergistic effect of Cr and Mo in case of Mo-containing alloys [1-3]. However, the specific roles of minor elements are not well understood especially with respect to precise location of Mo relative to the oxide/metal interface, nor the atomistic processes responsible for protective-oxide layer growth and breakdown. The composition, structure and thickness of the passivating oxide films are challenging to characterize considering their nanoscale dimensions and the high electric field imposed during growth in solution. Key processes that take place within the oxide and regulate passivation are controlled by defect interactions that are atomic, ionic, and electronic in nature and currently poorly understood, often needed to be studied at the resolution and detection limits of experimental methods [4]. Common electrochemical methods such as AC and DC electrochemistry are rarely connected with atomic scale *ex situ* techniques such as scanning tunneling (STM), atomic force (AFM) and transmission electron (TEM) microscopies to yield crucial information on structure, molecular and electronic properties of the oxides [5]. The main goal of this work is to integrate single crystal electrochemical measurements with nanoscale characterization to advance fundamental understanding and eventually predict the roles of Cr and Mo on surface stability in corrosive environments. Such a connection between global electrochemistry and atomic studies is infrequently reported [6].

Polycrystalline alloys contain many grain orientations that may affect passivation behavior [7]. This work focuses on examining the oxide growth kinetics on single crystals. It is expected that grain surface facet evolution and oxide thickness will vary according to crystallographic orientation [8, 9]. Model alloys Ni-22Cr and Ni-22Cr-6Mo, wt%, were arc-melted, cold-rolled to achieve ~12% deformation, and then heat treated to allow for re-crystallization and growth of sufficiently large grains to enable electrochemical measurements. A ~4 mm<sup>2</sup> area of a sample was first scanned with Electron Backscattered Diffraction (EBSD) to obtain a “catalog” of grain orientations, and then each grain within the EBSD map was probed regarding its electrochemical behavior.

The kinetics of the passive state of single grains were determined potentiostatically at +0.2 V<sub>SCE</sub> in solution, where a previously formed on air oxide was partially reduced at -1.3 V<sub>SCE</sub>. Electrochemical impedance spectroscopy (EIS) was then collected after various stages of oxide growth and the data was fit assuming a constant phase element to enable calculation of thickness [10]. Oxide charge formation, current density, and thickness for each alloy and grain orientation were studied using Mott-Cabrera and Point Defect models. *Ex situ* Raman and XPS conducted on polycrystalline samples aided in determining molecular identity and the efficiency of oxide growth versus dissolution.

AFM topography images and profiles across single grain surfaces at intermediate stages of potentiostatically controlled oxide growth were obtained to give insight on the nucleation and morphology of oxides formed on various grains. Furthermore, the structural and electrochemical properties of oxides grown potentiostatically on specific crystallographic orientations were correlated with the TEM analysis performed on the oxides grown chemically under equivalent conditions using potassium persulfate or hydrogen peroxide oxidants. It was found the EIS, TEM and XPS oxide thicknesses were in agreement with each other.

The broader relevancy of this presentation, besides connecting electrochemistry and nano- to mesoscale characterization, is its contribution to concepts beneficial towards development of predictive correlations associated with the passivity of Ni alloys during aqueous exposure.

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