

# Investigation of Initial Stages of Oxidation of Ni-Cr-Mo alloys by Scanning Tunneling Microscopy and Spectroscopy

G. Ramalingam, K.M. Lutton, K. Gusieva, J.R. Scully, P. Reinke

## Introduction

Ni-based alloys are commonly used in high temperature applications and in highly corrosive, aqueous environments due to their excellent corrosion resistance [1,2]. The presence of Cr (>13wt%) in these alloys enables the formation of an adherent Cr<sub>2</sub>O<sub>3</sub> passive layer which protects the underlying metal from further oxidation. Passivity and resistance to aqueous corrosion is also improved with additions of Cr, Mo and W [3]. Alloying minor amounts of Mo has shown to massively improve the localized pitting corrosion resistance in Fe-Cr-Mo and Ni-Cr-Mo alloys [3-5]. Potentiodynamic tests on Ni-Cr-Mo alloys in chlorine environments show that the amount of Mo plays a significant role in increasing the critical crevice potential [5]. A synergistic effect is often proposed between Cr and Mo; however, the exact role played by Mo in improving the resistance in conjunction with Cr is not yet fully understood. This lack of understanding of the effect of the minor alloying elements remains one of the biggest challenges in the field of fundamental corrosion science and technology. Understanding early stage corrosion processes at the nanoscale in passivating systems and the effect of alloying elements in the formation or repair of the passive oxide layer will allow us to better tailor the materials system and obtain the best corrosion resistance.

The objective of the current work is to observe the initial stages of oxidation of the passivating Ni-Cr and Ni-Cr-Mo alloys and understand which of the elementary processes in the initial stages of the reaction are important in terms of the long term stability of the oxide. We will discuss the initial stages of oxidation with O<sub>2</sub> of model Ni-Cr thin films with variable Cr concentrations using scanning tunneling microscopy/spectroscopy (STM/STS). We subsequently describe the effect of Mo, a minor alloying element, on the progression of the initial stages of oxidation until a continuous ultrathin oxide layer has formed. These results are compared with corrosion studies of ultrathin oxides grown electrochemically with acidic and alkaline solutions.

## Experimental Details

The Ni-Cr and Ni-Cr-Mo alloy thin films are prepared by electron beam evaporation of parent metals (Ni, Cr and Mo) in an UHV preparation chamber (base pressure  $<3 \times 10^{-10}$  mbar). The films are grown on MgO(001) substrates. The deposition conditions were optimized to yield the smoothest films and two recipes were developed to produce suitable and representative model surfaces: (a) deposition at 100 °C and subsequent anneal at 300 °C for 2 hours, and (b) deposition at 400 °C with no post-growth annealing. The targeted concentrations are 13-25 wt%Cr and 2-12wt% Mo. The preparation chamber is coupled to the STM which allows for in-situ preparation and oxidation of thin films in a highly controlled environment. Imaging and spectroscopy are performed with electrochemically etched W tips. The oxidation is performed by backfilling the chamber with O<sub>2</sub> to the required partial pressure and the amount of O<sub>2</sub> used in the oxidation experiments is described in Langmuirs (1 L = 10<sup>-6</sup> mbar-s).

In STS, we record I-V curves and the normalized differential  $[(dI/dV)/(I/V)]$  yields information of the local density of states (LDOS) of the system [6]. This information can be used to differentiate the initial

metallic surface from the oxides that form on the surface after oxidation. Different oxides that may form (including but not limited to  $\text{Cr}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{NiCrO}_4$ ,  $\text{MoO}_2$ ) can be differentiated by their bandgap value, topographic structure or by characteristic features in their LDOS. In addition, we record STS-maps, which are an array of  $103 \times 103$  differential conductance spectra ( $dI/dV$ ), and illustrate the spatial distribution of oxide islands which gives us information on their nucleation and growth on the surface.

The STM studies of Ni-Cr-Mo alloys surfaces is combined with the investigation of ultrathin oxide films grown chemically on bulk alloys samples. They will be grown in acidic solutions containing small concentrations of ferric chloride and ferric sulfate for controlled chemical passivation. The solutions of interest are:  $0.01 \text{ M HCl} + x \text{ M FeCl}_3 + y \text{ M NaCl}$  and  $0.01 \text{ M H}_2\text{SO}_4 + x \text{ M Fe}_2(\text{SO}_4)_3 + y \text{ M Na}_2\text{SO}_4$  (sodium salts may be added to control the conductivity of the electrolyte. The native oxide on the surface is reduced potentiostatically and the sample is then allowed to passivate in an aerated cell at open circuit potential. Once the potential reaches the passive region values, impedance scans will be performed to calculate the overall oxide film thickness.

## Results

Our preliminary data on the initial stages of oxidation of a Ni-13wt%Cr alloy surface at  $300 \text{ }^\circ\text{C}$  ( $0.5 \text{ L O}_2$  at  $10^{-9} \text{ mbar}$ ) indicate that nanometer sized oxide islands preferentially nucleate at step edges. At this stage, the step edges are still visible and the terrace structure of the metallic alloy surface is retained. However, the  $dI/dV$  values from the oxidized surface are lower in comparison to the starting metal surface (recorded at same voltage) which indicates a possible oxygen-chemisorbed structure on the terrace with oxide nuclei only found at the step edges. The transition from the chemisorbed state to the oxide therefore starts at the step edges. Subsequent oxidation ( $25 \text{ L of O}_2$ ,  $10^{-8} \text{ mbar}$  at  $300 \text{ }^\circ\text{C}$ ) results in a fully formed oxide layer accompanied by a complete loss in the step edge structure.

STS maps after  $25 \text{ L}$  oxidation indicate a continuous oxide layer and extracted spectra show the presence of a bandgap throughout the surface. The observed bandgap of  $1.42 \text{ eV}$  is less than the bulk bandgap of Ni and Cr-oxides and this observation is common in ultrathin oxide layers due to a high number of defects, coupling to the metal surface, or significant structural modification of the surface compared to the bulk phase. Oxidation studies on pure Ni and Cr thin films also show similar results: STS maps after oxidation at  $200 \text{ }^\circ\text{C}$  in excess of  $10 \text{ L}$  always show the presence of a complete oxide layer but the bandgap value does not correspond to the bulk oxides.

With these model experiments, we have (a) optimized thin film growth on MgO to obtain the smoothest films with largest possible terraces for variable alloy compositions, (b) studied the structure of pure Ni and Cr thin films and their oxidation behavior – this will serve as a platform to sequentially investigate the effect of Cr and Mo addition on the thin film structure and oxidation behavior, and (c) observed the initial stages of oxidation of Ni-13wt%Cr thin film and determined that the oxide phases initially start to form at the step edges.

## Research in Progress

We are currently working on room temperature adsorption experiments (submonolayer regime) to understand the chemisorption of oxygen on the Ni-Cr alloy (13-25wt%) surfaces. The subsequent annealing experiments will provide information on the role of surface reconstruction and rearrangement

on the transition from chemisorbed structure to oxide nucleation (and growth). The stability of the chemisorbed structure as a function of temperature (reaction progression to form oxides) and as a function of coverage (partial pressure of O<sub>2</sub> and exposure time) will be discussed. The transition from the chemisorbed structure to the oxide nucleation is one of the critical steps in the growth of the oxide layer and we will study the effect of Mo on this transition. Subsequently, we will present STM/STS data from single step, high temperature oxidation of Ni-Cr and Ni-Cr-Mo alloys as a function of oxygen partial pressure and exposure time. Cyclic polarization (CP) tests will be performed on the thin film samples and the effect of Mo on the corrosion behavior will be discussed and compared to the data from bulk alloy samples.

The nanoscale and mesoscale morphology and electronic structure of electrochemically prepared ultrathin oxide films will be compared with the oxides grown in the highly controlled UHV environment. This allows to draw conclusions on the dominant reaction pathways, which can be expressed in the structural characteristics studied with STM and STS.

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