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Kinetics of cathodic reduction of oxygen on Ni-Cr-Mo-W alloy.

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Ni-Cr-Mo-W alloys (C-group alloys) are well known as materials with very high corrosion resistance in very aggressive environments, an asset that has motivated the selection of Alloy 22 as a waste package material in the Yucca Mountain Project for the long-term geologic disposal of spent nuclear fuel and other high-level radioactive wastes. The aim of this project is to elucidate the corrosion performance of Alloy 22 under aggressive conditions and to provide a conceptual understanding and parameter data base that could act as a basis for modeling the corrosion performance of waste packages under Yucca Mountain conditions.

A key issue in any corrosion process is whether or not the kinetics of the cathodic reactions involved can support a damaging rate of anodic metal (alloy) dissolution. Under Yucca Mountain conditions the primary oxidant available to drive corrosion (most likely in the form of crevice, or under-deposit, corrosion) will be oxygen. Here, we present results on the kinetics of oxygen reduction at the Alloy 22/solution interface.

Conventional electrochemical techniques (potentiostatic current transients, cyclic voltammetry, and electrochemical impedance spectroscopy (EIS)) as well as surface analytical techniques (X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectroscopy (ToF SIMS)) have been employed to investigate the properties of the oxide film on the C22 surface. Experiments were performed in oxygen saturated 5 M NaCl solutions at different temperatures (from 30°C to 90°C). Alloy 22 specimens were mechanically polished to a 2 μm finish. Initially present air-formed oxide layers were cathodically reduced at –1000 mV (vs. saturated silver-silver chloride reference electrode) for one hour. Then, an oxide film was electrochemically formed for one hour at different potentials (holding potentials) from -600 mV to 600 mV. A voltammetric scan was then run on the oxide-covered surface from the holding potential to –1000 mV to observe the currents for oxygen and water reduction. The following scan from –1000 mV back to the holding potential allowed us to determine whether oxide film reduction (at the negative potentials reached on the forward scan) influenced the oxygen reduction reaction kinetics.

Current transients (plotted in the log i vs log t format) recorded in the holding potential range, -600 mV to 0 - 200 mV, showed a current decrease with time consistent with the formation of a passive oxide. Under these conditions the voltammetric scans showed a very significant suppression of the oxygen reduction current. The current at a potential of –750 mV in the scan was used as an indication of the oxygen reduction current. This potential was shown to be in the limiting current region for this reaction. The change in this current as a function of holding potential is shown in Figure 1. For holding potentials in the range 0 mV to 600 mV the current transient behavior at the holding potential and the current density for oxygen reduction varied depending on the temperature. At 30°C, 70°C and 90°C the current has only a minor dependence on holding potential. By contrast, over the same potential interval at 40°C and 50°C, an increase in holding potential causes the absolute value of current to increase. Based on the Point Defect Model [1] this increase in current can be attributed to an increase in the defect density in the oxide film. This is consistent with our EIS data, which show a significant decrease in film resistance at these potentials and temperatures.

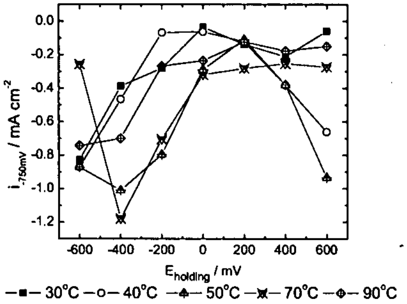

Figure 1. Current density for oxygen reduction (at –750 mV) as a function of holding potential at different solution temperatures.

Ex-situ XPS shows that at 30°C the film is comprised of 3 groups of compounds: 1) hydroxides of Cr and Ni and Mo in a high oxidation state ($Cr(OH)_3$, $Ni(OH)_2$, MoO_3); 2) Oxides and Mo in a lower oxidation state (Cr_2O_3, NiO, MoO_2); 3) metals (Cr, Ni, Mo). The relative amount of the metals goes down as the potential becomes more positive suggesting an oxide thickening. The amount of the first group of compounds rises with an increase in potential, while the amount of the second group of compounds has only a very minor potential dependence. The W data is not included since the 4f $_{7/2}$ photoelectron lines for W oxides overlap the Mo 4p photoelectron line. As a result, deconvolution of the W signal required XPS data for an alloy with no Mo. This work is planned in the near future.

ToF SIMS results show, that independent of holding potential at 30 °C, the film has two major layers. An outer layer consisting mainly of Mo and W compounds (up to 2 nm), and an inner layer build up from Cr and Ni compounds (up to 4 nm). The thickness of the oxide layer increases as the potential becomes more positive, consistent with XPS observations.

These results show that the composition, and perhaps also the thickness, of the oxide film on Alloy 22 have a significant effect on the alloys ability to support oxygen reduction. The influence of temperature on film properties, and, hence, on oxygen reduction kinetics is complex and remains to be elucidated.

Reference list

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