Evaluation of protective film on Ni-Cr-Mo-W alloy by electrochemical and surface analysis techniques.

D. Zagidulin, B. Sherar, P. Jakupi , J.J. Noël, D.W. Shoesmith.
University of Western Ontario

Western

MOTIVATION

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 candidate for waste package material in the proposed Yucca Mountain repository for the long-term geologic disposal of spent nuclear fuel and other high-level radioactive wastes.

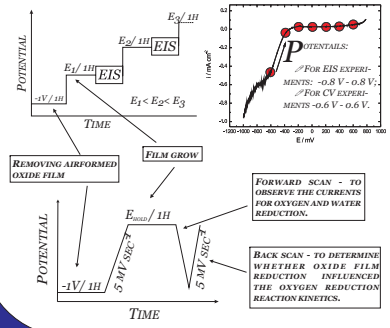
The aim of this project is to elucidate the corrosion performance of Alloy 22 under aggressive conditions and to provide a conceptual understanding and parameter data base that could act as a basis for modeling the corrosion performance of waste packages.

EXPERIMENT

Techniques used:

- ☑ Electrochemical
  - Electrochemical Impedance Spectroscopy
  - Current transients
  - Cyclic Voltammetry
- ☑ Surface analysis

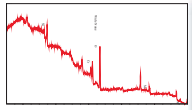
Solution - 5 mol/L NaCl. T = 25°C - 90°C. Solution was deaerated with argon or saturated with oxygen.



Potentials:
- For EIS experiments: -0.8 V - 0.8 V;
- For CV experiments -0.6 V - 0.6 V.

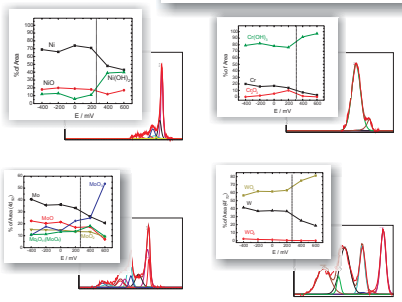
RESULTS AND DISCUSSION

X-ray Photoelectron Spectroscopy

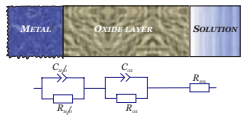


The ex-situ XPS data on the protective films formed at different holding potentials at 90°C, shown that at pH= 8 - 8.5 the protective layer consists of three groups of compounds:

1. Hydroxides of chromium and nickel, as well as the higher oxides of molybdenum and tungsten. Relative concentrations of the compounds increase mainly at formation potentials more positive than 0.2 V.
2. Oxides of nickel and chromium are mixed with lower oxides of molybdenum and tungsten. In this case, the relative concentrations of the compounds have very week dependencies on the potential.
3. Metallic nickel, chromium, molybdenum and tungsten. The concentrations of metals decrease with increasing potential, and change

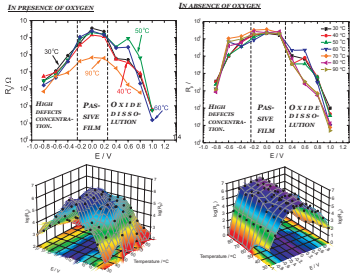


Electrochemical Impedance Spectroscopy

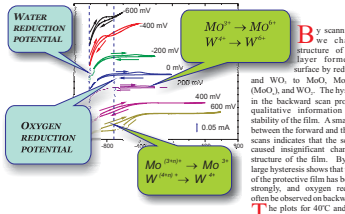


EIS data shows that film resistance depends on holding potential with maximum in potential interval -200 to 200 mV.

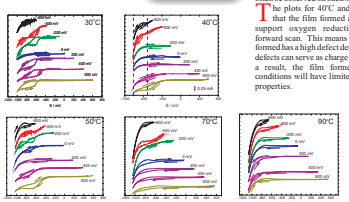
In presence of oxygen measured abolute impedance values are smaller in the range of oxygen reduction potentials.



Cyclic Voltammetry

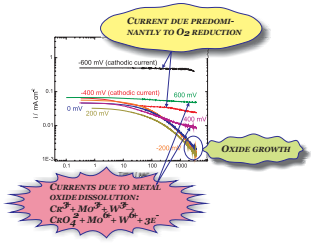


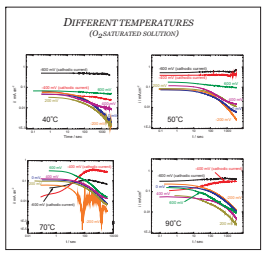
By scanning to -1 V we changed the structure of the oxide layer formed on the surface by reducing MoO_3 and WO_3 to MoO_2 MoO_x, Mo_2O_5, $(MoO_2)_x$ and WO_2. The hysteresis seen in the backward scan provides some qualitative information about the stability of the film. A small hysteresis between the forward and the backward scans indicates that the scan to -1 V caused insignificant changes to the structure of the film. By contrast, a large hysteresis shows that the structure of the protective film has been changed strongly, and oxygen reduction can often be observed on backward scan.



The plots for 40°C and 50°C show that the film formed at 0.6 V can support oxygen reduction on the forward scan. This means that the film formed has a high defect density and the defects can serve as charge carriers. As a result, the film formed at these conditions will have limited protective properties.

Current Transients





The transients obtained for the potentials -0.6 V and -0.4 V form a first group. For this group, negative current dominated because of the oxygen reduction reaction occurring at these potentials. Growth of the protective film was very limited.

A second group is formed by the transients obtained at -0.2V, 0V and 0.2V. A transients have a distinctive film growth shape after an initial horizontal region. The final current values for the transients from this group are the smallest of any in the whole set of applied potentials.

The transients obtained at 0.4 V and 0.6 V form a third group. Taking into consideration the XPS data, the current is mainly attributable to the following reactions:

$Mo^{3+} \rightarrow Mo^{6+} + 3e^{-}$

$W^{4+} \rightarrow W^{6+} + 2e^{-}$

$Cr^{3+} \rightarrow Cr^{6+} + 3e^{-}$

as well as chromium and nickel hydroxide formation. It is known that the oxides with high oxidation numbers can support anion charge transfer through the film.

SUMMARY

EIS data shows that film resistance depends on holding potential with maximum in potential interval -200 to 200 mV;

Cyclic voltammograms show that Alloy 22 can support oxygen reduction reaction on the surface at some conditions;

XPS data shows 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.

We wish to note that the EIS data, the data obtained from the current transients, and the CV data are in good agreement. They show that the oxide film formed at holding potentials between -0.2 V and 0.2 V has the strongest protective properties. The concentration of defects in films formed at more negative potentials was higher and the film had lesser protective properties. At more positive film formation potentials, Mo^{6+} and W^{6+} can serve as catalysts of the oxygen reduction reaction. In conjunction with Cr^{6+} formation by oxidizing protective Cr_2O_3 this can enable a situation in which the oxygen reduction reaction (cathodic half-reaction) is possible. As result, the anodic half-reaction (corrosion) will take place as well.

ACKNOWLEDGMENTS

We are grateful to Surface Science Western for surface analyses.

The support of this work from the Office of Science and Technology and International (OST&I), Office of Civilian Radioactive Waste Management (OCRWM), U.S. Department of Energy (DOE) is gratefully acknowledged. The work is carried out as part of the DOE Multi-University Corrosion Cooperative under Cooperative Agreement DE-FC28-04RW12252.

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