University of Toronto – Roger C. Newman IRC

UNENE/NSERC IRC Program: Corrosion Control and Materials Performance in Nuclear Power Systems

Overview

This IRC program is in its third 5-year term, which began in September 2014. The research focuses on mechanisms, prediction and control of metallic corrosion, with ancillary activities such as studies of hydrogen in pressure tube material and electrochemical condition monitoring generally. The materials studied range from industrial alloys through pure laboratory melts.

The IRC research takes place alongside studies of copper corrosion relevant to nuclear waste disposal, funded by NWMO and recently augmented by a new ORF program based at Western University. Roger Newman also held NSERC Discovery and Discovery Accelerator grants for research in nanoporous metals.

2017-2018 Highlights

Collaboration with the CCEM, McMaster University, and former PhD student Suraj Persaud and CNL colleagues continued, while increased use was made of advanced methods in the OCCAM facility at UofT. In January 2018, Suraj joined Queen’s University as Assistant Professor, and there are plans for an eventual succession in the corrosion area over the next decade. We continue to seek high-quality output in the high-resolution characterization of cracks and surface corrosion, using analytical electron microscopy and atom-probe tomography (APT). A number of MASc students have been working on a diverse range of topics, including lead effects on corrosion, internal oxidation, and the stability of sulfate in steam generator crevice environments (and the effects of the resulting reduced sulfur species). A localized corrosion modeling activity, started early in 2017, continued – specifically directed at phenomena relevant to nuclear steam generators, but also with a broader strategic aim of making the group self-sufficient in reaction-transport modeling. Other new projects involve dealloying of Monel, molten-salt corrosion relevant to SMRs, and revisiting the concentration of corrodents in steam-generator crevices and deposits.

The high-resolution characterization of cracks and surface corrosion is of keen interest to industry, especially the achievement of relatively routine cross-sections of crack tips and subsequent TEM study. In the coming years, such studies will become routine for the analysis of plant artefacts, a huge leap forward from the conventional SEM era.

There are strong synergies between the IRC research and the group’s research on functional nanoporous metals. Former PhD student Ayman El-Zoka, now at the University of Antwerp, has published extensive APT and TEM studies of such materials, which can lead to superior methods for nanoscale study of important plant-related phenomena (see for example Nanoscale, 10, 4904–4912 (2018)).
Some specific highlights are now presented. In collaboration with Suraj Persaud and the CCEM, PhD student Mariusz Bryk has obtained a new level of resolution in the analytical TEM of stress corrosion crack tips in Alloy 800 – **Figure 1**. Depending on the age of the crack tip being examined, there are either lumpy enrichments of metallic Ni, as observed previously for “old” crack tips (crack on the right), or an extremely fine nanoporosity that must be the triggering factor in crack extension for “fresh” crack tips (crack on the left) –

**Figure 1**

MASc student Hao Zhu made further progress in the understanding of the resistance of Alloy 690 to stress corrosion cracking in primary water (PWSCC). **Figure 2** shows the typical appearance of the alloy surface after exposure to a simulated PWSCC environment. The nodules within the grains are Ni, expelled by internal oxidation of Cr, just as we observe in Alloy 600, as first shown by Persaud a few years ago, but near the grain boundaries we see a protective Cr-rich oxide. We have gone back and forth in the interpretation of this observation, but Hao has now performed an analytical TEM study - **Figure 3** - that takes us closer to a convincing resolution of the issue. Near the grain boundary, which is just out of view on the right side of the image, internal oxidation occurs, just as within the grain, but after a while a healing layer of oxide forms at the boundary of the internal oxidation zone around the grain boundary and the intact alloy (bright lines in Cr and O on the right-side of the image). This seems to be due to lateral expulsion of Ni towards the grain boundary, adding to its expulsion to the surface and facilitating beneficial Cr oxidation. External Ni nodules form at first, but then stop growing.

Hao Zhu also did similar experiments on model alloys close to the 690 composition, prepared with our cold-crucible melter. Alloys with 30 and 35% Cr were compared. Remarkably, even the 35% Cr alloy showed internal oxidation within many grains, but it showed a higher proportion of grain surfaces (close to {100} planes) that showed protective external oxide.
Figure 2

(d) Chromium

(c) Nickel

(f) Iron

(g) Oxygen

Figure 3

Manganese

Aluminum
The Research Group and its Facilities

As of April 2018, the group consisted of 6 PhD students, 3 MASc students, 2 postdoctoral fellows, and one Senior Research Associate. Several undergraduates and MEng students also contributed over this reporting period. About 2/3 of this effort was supported by the IRC program.

The group is well equipped for electrochemistry and microscopy, including atomic force microscopy, and has a growing facility for high-temperature, high-pressure testing in water, steam or aqueous solutions. An Arcast cold-crucible induction melter is now in regular use for preparation of model alloys. We increasingly exploit the local OCCAM facility for electron microscopy and surface science. Particular students are being trained to use some of the advanced methods personally.

Three recent PhD graduates (Adrian Vega, Jagan Ulaganathan, Suraj Persaud) were working at Canadian Nuclear Laboratories, until Persaud joined Queen’s University as Assistant Professor in January 2018. Numerous alumni work for OPG.

Examples of Specific Industry Interactions

There has been continuing consulting assistance to OPG in the area of electrochemical monitoring in reinforced concrete for life prediction of dry storage containers for used nuclear fuel. The contractor started site work at the Darlington WMF in 2012, and data are being analyzed as they are produced. Miscellaneous assistance was given in areas such as dealloying of Monel and corrosion of Alloy 600.

Concrete collaborations are under way with CNL, specifically with Jared Smith, and this will be a growth area in the next few years.

Public Output

Invited presentations were given at the Canadian Materials Science Conference in Ottawa, the 100th Canadian Chemistry Conference in Toronto, an ASTM symposium on Advances in Electrochemical Techniques for Corrosion Monitoring in Atlanta, FIMPART 2017 in Bordeaux, the NACE annual conference in Phoenix (presented by Persaud – memorial symposium for Roger Staehle), and at Aalto University (Finland). Several contributed talks and posters were presented nationally and internationally.

Publications arising from the IRC program included the following –


