Corrosion Studies of Alternative Filler Materials for Manufacturing CANDU® Brazed Joints

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Summary

Currently, beryllium is used as a filler material to braze appendages to CANDU® fuel sheaths. Due to toxicity concerns, the possibility of using alternative filler materials is being investigated. Several materials have been proposed and now must be tested to determine their suitability for implementation. As part of this testing, the corrosion resistance of each potential material must be evaluated. This work includes thermodynamic modelling to predict corrosion susceptibility of alternative material brazed joints, and experiments to determine corrosion properties in conditions simulating reactor shutdown.

1. Introduction

Two types of appendages are attached onto CANDU fuel sheaths: spacers and bearing pads. Spacers are small Zircaloy-4 (Zr-4) pieces, which are attached at the axial centre of each element. The spacers ensure that the separation between elements is maintained [1]. Larger Zr-4 appendages called bearing pads are attached to the exterior elements of the fuel bundle. These allow the bundle to slide within the pressure tube and maintain the designed geometry of the bundle within the fuel channel. Specifically, they position the fuel bundles such that the fuel sheaths do not contact the pressure tube. This limits heat transfer between the bundle and pressure tube. Both appendages are shown in Figure 1.

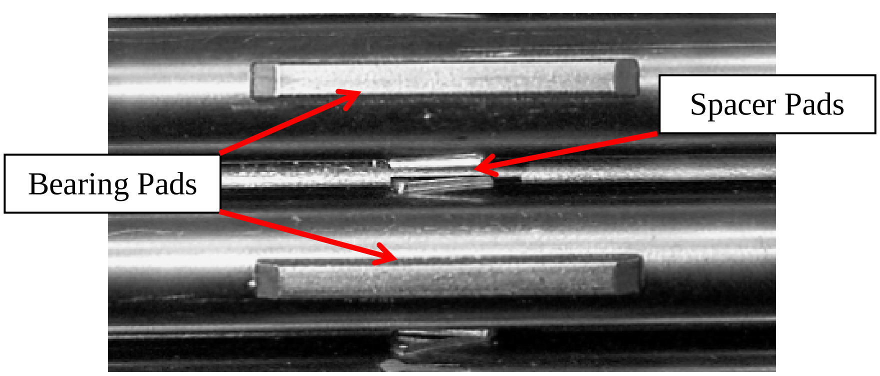

Figure 1- Bearing pads and spacers attached to fuel sheathing [1].

Both of these appendages are attached to fuel sheaths using a brazing process, with beryllium (Be) as the filler material. This process can create airborne beryllium oxide particulates, which are a health hazard to workers in the manufacturing environment. To address these concerns, the Ontario Ministry of Labour is expected to adopt a 40-fold reduction in the allowable limit on airborne Be particulates [2]. This could interfere with CANDU fuel manufacturing, as current methods may have difficulty achieving compliance with the new regulations. In anticipation of this change, a CANDU Owners' Group (COG) initiative has been launched to investigate the use of alternative filler materials to replace beryllium [3]. Within this initiative, extensive testing of alternative material brazed joints is required. This includes evaluations of joint constructability, mechanical strength, corrosion resistance, high temperature behaviour, and behaviour under irradiation.

This work focuses on the evaluation of corrosion resistance of alternative material brazed joints. Specifically, thermodynamic models will be generated to predict the corrosion susceptibility of each alternative material alloy. These models will be supported by experimental investigations of the corrosion resistance of each alloy in conditions characteristic of a reactor outage. The results of these corrosion studies will assist in determining the most promising candidate brazing material.

2. Modelling of Corrosion Behaviour

Thermodynamic models may be used to predict the equilibrium aqueous species concentrations that result when a material is immersed in water at varying: (i.) pH, (ii.) reduction potential, (iii.) pressure, and (iv.) temperature conditions. Based on the predominant aqueous species, conditions of immunity, passivity, and corrosion susceptibility may be predicted. Models based upon the work of Pourbaix will thus be developed to predict the corrosion behaviour of each alternative material alloy to assist in determining each alloy's suitability for replacing beryllium as a filler material in CANDU brazed joints.

2.1 Theory

Marcel Pourbaix (1904-1998) was a Belgian chemist most well-known for the derivation of reduction potential (E) – pH relations and diagrams (Pourbaix digrams) [4]. A Pourbaix diagram plots the stable equilibrium phases of an aqueous system as a function of reduction potential and pH [5]. These plots may be used to predict corrosion susceptibility.

Corrosion occurs by electrochemical processes, which are described by the generic reaction (Eq.1), where R is a solid reactant, P is an ionic product in solution, H^+ is the hydrogen ion in solution, and e^- are the free electrons. The symbols *r*, *w*, *x*, *h*, and *n* represent the reaction coefficients for the corresponding reactants and products.

$$rR + wH_2O \rightarrow xP + hH^+ + ne^- \tag{1}$$

The equilibrium reduction potential is given as a function of the concentrations of participating species by the Nernst equation (Eq. 2):

$$E = \frac{\Delta G^\circ}{nF} + \frac{0.0591}{n} log \frac{(a_P)^x (a_{H+})^h}{(a_R)^r \left(a_{H_2O}\right)^w} \tag{2}$$

where E is the reduction potential, $\Delta G°$ is the standard free energy change of the reaction, F is Faraday's constant, a is the activity of species involved, and n is the number of free electrons. As the activity of H_2O is necessarily equal to 1 (*e.g.*, $a_{H_2O} = 1$), reactant R is assumed solid (*e.g.*, $a_R = 1$). Recalling that $pH = -\log(a_{H^+})$, the Nernst equation may be rewritten as:

$$E = \frac{\Delta G°}{nF} + \frac{0.0591p}{n} log(a_P) - \frac{0.0591h}{n} \mathrm{pH} \quad (3)$$

Using tabulated data to calculate the standard free energy change for the reaction, Eq. 3 can be used to determine aqueous species activity as a function of reduction potential and pH. To calculate this at elevated temperatures, the standard Gibbs free energy of the reaction ΔG must be known for the specified temperature. For most reactants, the Gibbs energy of formation $G°$ is known for standard ambient conditions (298 K, 1 atm), so the Gibbs energy at elevated temperatures (G_T) must be calculated.

If thermodynamic data (e.g., H^o_{298K}, S^o_{298K} and constant pressure heat capacity (c_P)) are known, then the G_T (Eq. 4) can be calculated for all involved species [6].

$$G_T = H^o_{298K} + \int_{298}^{T} C_P dT - T\left(S^o_{298K} + \int_{298}^{T} \frac{C_P}{T} dT\right) \quad (4)$$

Subsequently, the ΔG for the dissolution reaction (Eq.1) can be determined and the equilibrium species activity may be calculated using Eq. 3. It is noted that the above process does not consider pressures above 1 atm, as pressure causes only a small variance in enthalpy or entropy values between 1 and ~100 atmospheres [7].

2.2 Corrosion Modelling using Computational Thermodynamics

Based on the theory described, thermodynamic models of the aqueous systems will be generated for each alloy in order to predict corrosion behaviour. These will incorporate the multiple reactions possible between components of each alloy and water, and will allow the determination of species predominance at elevated temperatures as a function of pH and reduction potential.

A computational thermodynamic modelling software package that utilizes Gibbs energy minimization and an extensive thermodynamic database will be used to create these aqueous models. These models predict the most thermodynamically favourable reactions, as well as the resulting equilibrium aqueous species concentrations as a function of pH and reduction potential.

It is noted that equilibrium modelling does not necessarily represent the real aqueous species concentrations of the braze alloy systems. Depending on kinetics, a real system may not reach these predicted dissolved species activities. Experiments will be completed to compare real aqueous species concentrations to those predicted by thermodynamic modelling.

3. Corrosion Testing Experiments

Experiments to investigate the corrosion resistance of alternative material alloys at varied conditions are required within the Be Replacement Material Qualification plan. At RMCC, experiments will be performed to evaluate the corrosion resistance of each material at conditions characteristic of a reactor shutdown; this is intended to complement operational conditions testing being performed by other project collaborators. Additionally, results will be compared to modelling predictions. An experiment plan and apparatus have been designed, and experiments will begin over the summer of 2014.

3.1 Experiment Plan and Apparatus

The *shutdown conditions* corrosion experiment is intended to simulate an extended reactor outage. In this situation, coolant temperatures are lower than during operation, but conditions may be more oxidizing. Specifically, samples of bearing pad joints constructed with different filler materials will be exposed to water at 40-90°C, pH 7-8, Li (as LiOH) concentration of 0.5 ppm, and dissolved oxygen concentrations up to 3 ppm, for a period of 50 days. The bearing pad samples will then be removed, and properties including weight change, oxide thickness (on the braze alloy, bearing pad, and fuel sheath), hydrogen uptake (of the sheath and bearing pad), braze alloy degradation, and mechanical strength will be evaluated. This will be used to assess potential corrosion effects on the integrity of the alternative material brazed joints and surrounding sheath area.

An apparatus has been designed to accomplish this experiment (Figure 2 and Figure 3). The brazed joint specimens will be held within a Teflon sample holder, to keep samples electrically isolated from each other. The sample holder will sit within a sealed Pyrex vessel, containing an inert FEP (fluorinated ethylene propylene) liner to prevent test liquid contamination.

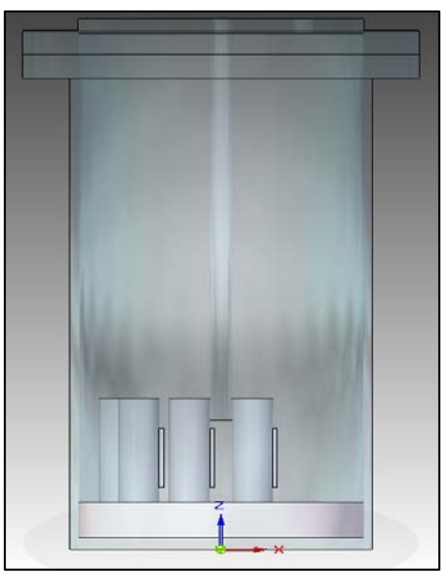

Figure 2- CAD model of the corrosion test apparatus.

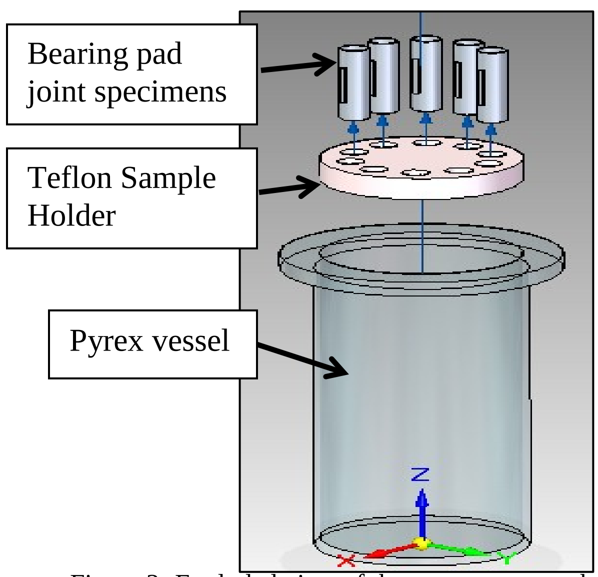

Figure 3- Exploded view of the test apparatus, showing the glass vessel, Teflon sample holder, and brazed bearing pad specimens.

After the experiment, inductively coupled plasma mass spectrometry (ICP-MS) analysis will be performed to measure the concentration of species that may have leeched from the braze alloy into the test liquid. These results will be compared to aqueous species predictions from thermodynamic modelling activities.

4. Conclusion

A plan for corrosion studies of alternative filler material alloys has been presented. This includes the development of thermodynamic models to predict the aqueous system behaviour of each alloy, as well as shutdown conditions corrosion experiments. An initial review of aqueous system modelling has been undertaken, and models are expected to be completed over the summer of 2014. An apparatus for corrosion testing of CANDU braze alloys have been developed, and experiments will proceed through the summer and fall of 2014. The results of these studies will contribute to the assessment of alternative materials to replace beryllium as a filler material in CANDU brazed joints.

5. Acknowledgements

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6. References

[1] Manzer, A. "Introduction to CANDU Fuel", Presented to USNRC, Washington, DC. 4 September 2003. Available at <http://pbadupws.nrc.gov/docs/ML0325/ML032530144.pdf>

[2] "Alert: Workplace Beryllium Exposure". Ontario Ministry of Labour, November 2010. Available at <https://www.labour.gov.on.ca/english/hs/pubs/alerts/a21.php>

[3] E.C. Corcoran, T. Daniels, J. Harmsen, E. Lu, S. Palleck, A. Pant, T. Onderwater, and F. Dimayuga, "Status of The Beryllium Replacement Project", Presentation at the 12th International Conference on CANDU Fuel, Kingston, Ontario, Canada, 15-18 September 2013.

[4] Pourbaix, M. "Atlas of Electrochemical Equilibria", National Association of Corrosion Engineers, 1974.

[5] Verink, E.D. "Simplified procedure for constructing Pourbaix diagrams", *Uhligs Corrosion Handbook*, 2011.

[6] M. Moran, H. Shapiro, D. Boettner, M. Bailey. "Fundamentals of Engineering Thermodynamics", John Wiley and Sons, 1 Dec, 2010.

[7] M.H. Kaye and W.T. Thompson, "Chapter 9: Computation of Pourbaix diagrams at elevated temperature," in *Uhlig's Corrosion Handbook*, 3rd ed., R. W. Revie, Ed. The Electrochemical Society, 2011.