Modelling the Long-term Corrosion Behaviour of Candidate Alloys for the Canadian SCWR

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Summary

Corrosion behaviour of Inconel 625 and Incoloy 800H, two of the candidate fuel cladding materials for Canadian supercritical water (SCW) reactor designs, were evaluated by exposing the metals to SCW in UNB's SCW flow loop. Individual experiments were conducted over a range of 370^{o}C and 600^{o}C. Exposure times were typically intervals of 100, 250, and 500 hours. Experimental data was used to create an empirical kinetic equation for each material. Activation energies for the alloys were determined, and showed a distinct difference between low-temperature electrochemical corrosion mechanism and direct high-temperature chemical oxidation.

1. Introduction

Research is currently underway to create the next generation of nuclear plants through the Generation IV International Forum (GIF). Canada has chosen to participate in GIF by investigating one of the most promising designs: the SCWR (Supercritical Water-Cooled Reactor). UNB Fredericton has been a part of this research, and has investigated over a dozen alloys and potential protective coatings for use in the Canadian SCWR. Reported here are the results obtained when assembling the kinetic model for Inconel 625 and Alloy 800H, two candidate materials for fuel cladding, as compiled from numerous tests conducted at UNB.

2. Test Methods

The test loop at the University of New Brunswick was constructed to simulate the conditions under which the Canadian SCWR is expected to operate. Metal coupons were progressively polished to 600-grit silicon carbide paper, were stamped, and then washed with in an acetone sonic bath. The majority of experiments were performed with approximate exposure times of 100, 250, and 500 hours within UNB's SCW loop at temperatures of 370, 400, 500, 550, and 600^{o}C. System pressure was maintained at 25 MPa via a constant displacement pump and a regulating needle valve. During operation water is heated (and later cooled) in a tube-in-tube heat exchanger, and reaches the operating temperature via an electric heater. Water enters and exits the autoclave in which coupons are housed, and is cooled via the tube-in-tube heat exchanger followed by a chilled water shell and tube heat exchanger.

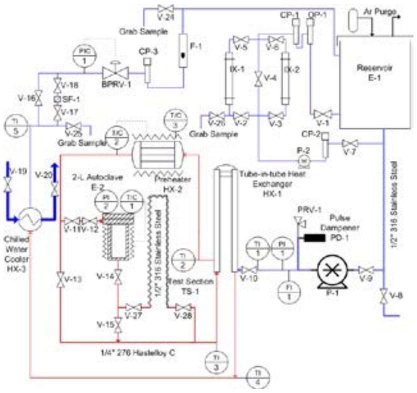

Figure 1 - UNB SCW Test Loop Schematic

Coupons were weighed before the start of each experiment and after each exposure time checkpoint, and at least one coupon was removed for surface characterization (SEM, TEM, etc.). While most samples were eventually descaled to determine the true corrosion rate, the results presented here are of direct weight change of coupons over time.

3. Results & Discussion

The average weight change over time was used to create a linear fit, where the slope of the line gives the specific kinetic constant describing the weight change of the alloy at the experimental temperature. Although all experiments were not conducted under the same concentration of dissolved oxygen in the system, the specific kinetic constants for experiments conducted at the same temperature were considered equivalent and averaged to give a value for each temperature, neglecting the effect of dissolved oxygen.

Table 1. Experimental kinetic constants for each experiment run.

Experiment	Temperature (^oC)	- k (I625)
U	370	0.00798
F	400	0.00119
K	400	0.00932
G	500	0.00413
E	550	0.00597
P	550	0.01125
Q	600	0.01727

Additional data was obtained from literature in order to give a second data point for weight change of Inconel 625 in subcritical water. The weight change was described by a parabolic function that was used to determine the lower-temperature weight change as at 500 hours of exposure [1]. The kinetic constants used to formulate the models for I625 and A800H are shown in Table 2:

Table 2 - Averaged experimental kinetic constants at each temperature

Temperature (°C)	Average (- k) (I625)	Average k (800H)
260 / 305	0.00331(Ziemniak)	0.006 (Alverez)
370	0.00798	0.01293
400	0.00525	0.01408
500	0.00413	0.01619
550	0.01011	0.02953
600	0.01727	N/A

The negative, averaged kinetic constants for I625 were used to derive an Arrhenius plot to determine the activation energy and pre-exponential factor for I625 oxidation. The Arrhenius plot is shown in Figure 2 and suggests two separate oxidation mechanisms with an inflection point in the corrosion rate just past the pseudo-critical transition. This phenomenon has been described previously in literature [2] [3]. It is attributed to the differences between the electrochemical corrosion (EC) of the alloy at sub-critical conditions versus the direct chemical oxidation (CO) mechanism at elevated, supercritical temperatures. The overall kinetic constant can be described by the equation:

$$k_{app} = k_{EC} \exp\left(-\frac{E_{EC}}{RT}\right) C_{H^+} + k_{CO} \exp\left(-\frac{E_{CO}}{RT}\right) \quad \textbf{(1)}$$

where k_{app} is the apparent specific rate as determined through the corrosion experiments presented above (dW/dt), E_{EC} is the low-temperature activation energy (electrochemical) and E_{CO} is the high temperature activation energy (for the direct chemical oxidation term). The terms k_{EC} and k_{CO} are the frequency factors for the EC and CO mechanisms respectively. The term C_{H+} is the concentration of hydrogen ions (mol/kg), which was calculated for neutral conditions from the ionization constant of water.

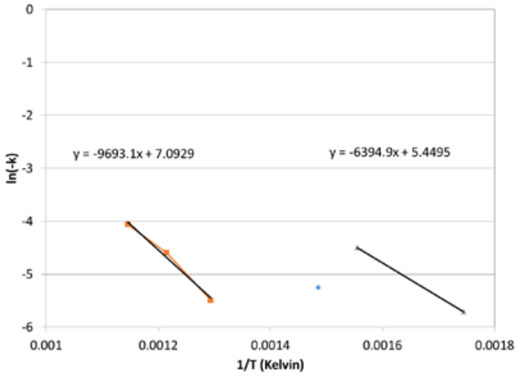

Figure 2 - Arrhenius plot of I625 oxidation indicating separate oxidation mechanisms.

The above equation was used with the observed experimentally determined kinetic constants to describe the processes involved. The high temperature activation energy due to direct chemical oxidation was derived through the slope and intercept over the data range of 500-600°C where it is assumed that the electrochemical oxidation term would be negligible. The activation energy and pre-exponential factor for I625 oxidation were determined to be:

E_{CO} = 80.6 kJ/mol
k_{CO} = 1201 mg/dm^2.hr^{-1}

The apparent rate constant at 400°C is likely a combination of the EC and CO terms. In order to separate the electrochemical term from the oxidation term data, results from Ziemniak and Hanson [1] at 260°C were used to estimate the kinetic constant in lower temperature sub-critical water. The resulting parameters were determined for the EC mechanism for I625:

E_{EC} = 51.2 kJ/mol
k_{EC} = 1.151 x 10^8 mg/dm^2 kg/mol hr^{-1}

Formulating these kinetic parameters into the corrosion rate equation results in the following equation describing the weight change of the alloy over time:

$$\Delta W = \left\{ k_{EC} \exp\left(-\frac{E_{EC}}{RT}\right) C_{H^+} + k_{CO} \exp\left(-\frac{E_{CO}}{RT}\right) \right\} \Delta t \ \text{ mg/dm}^2 \qquad \textbf{(2)}$$

The below figure shows the modelled effect of temperature on weight loss of I625 over a period of 500 hours along with the averaged weight loss values derived from the experiments at UNB. A similar approach was taken for the Alloy 800H data set and the modelled effect as a function of temperature with the 500 hour data is shown in Figure 3.

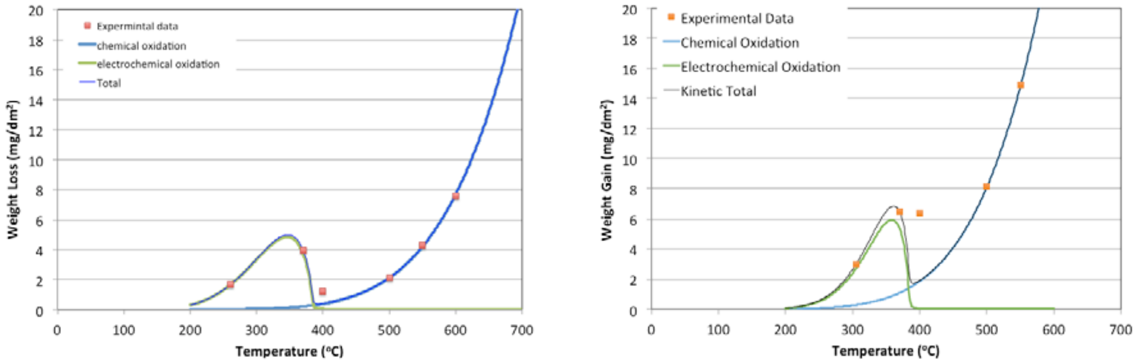

Figure 3- Experimental and modeled corrosion rates of I625 and A800H

The results of the analysis for Alloy 800H indicated the following activation energies and frequency factors for the CO and EC terms:

E_{CO} = 63.6 kJ/mol
k_{CO} = 321.6 mg/dm^2.hr^{-1}
E_{EC} = 81.0 kJ/mol
k_{EC} = 4.259 x 10^{10} mg/dm^2 kg/mol hr^{-1}

The model fits the experimental values reasonably well and demonstrates the local maximum in oxidation rate around the supercritical point. This occurs in the case of weight loss and weight gain as shown for I625 and 800H respectively.

Results indicate that I625 experiences less weight change than Alloy 800H over time. When results are extended to the estimated life time of Canadian SCWR fuel rods (30 600 hours), the results give a penetration into the fuel rod material of 0.0506 mm and 0.0986 mm for I625 and 800H respectively, where both materials meet the maximum tolerance of 0.2 mm for the cladding.

4. Conclusions

Gravimetric data for Inconel 625 and Alloy 800H were collected from experiments performed in the UNB SCW corrosion test loop and from compiled literature sources. The data was used to evaluate kinetic parameters for the general corrosion or oxidation of the alloys and Arrhenius plots revealed the separation of oxidation mechanisms. The results demonstrated a local maximum in corrosion rate is obtained around the critical point and that the overall alloy corrosion rate increases with increasing temperature, as would be expected.

5. Acknowledgements

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6. References

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