Mapping the Zirconium-Hydrogen Phase System

by

James Leigh McLean Corrigall

A Thesis submitted to
the Faculty of Graduate and Postdoctoral Affairs
in partial fulfilment of the requirements for the degree of

Master of Applied Science
in
Materials Engineering

Ottawa-Carleton Institute for Mechanical and Aerospace Engineering

Carleton University
Ottawa, Ontario

© 2018

James Leigh McLean Corrigall

leigh.corrigall@carleton.ca

October 5, 2018

Abstract

There are economic incentives to extend service of CANDU nuclear reactors in Ontario because of their reputation for safety and reliability. Pressure tubes made of zirconium alloys are vulnerable to failure by Delayed Hydride Cracking (DHC), which limits the amount of hydrogen, stress, temperature, and service life. Recreating reactor end-of-life conditions for testing purposes requires a method of adding hydrogen quantitatively into zirconium alloys without modifying irradiation damage.

The thesis demonstrates a promising mechanical hydriding technique that is suitable for adding hydrogen beyond the conventional solubility limit into zirconium alloys at 200 °C within hours, with 99 % accuracy and 3 % precision based on mass-balance. The technique can be used to map the Zirconium-Hydride phase system. Results attributed to the delta (δ -ZrH_x) solvus have been measured and agree with reported values. Confidence in the model is reinforced by the determination of hydrogen solubility in a copper barrier, which was found to agree with theoretical predictions.

Einstein-McRae-Coleman-Cottrell (EMCC) model predictions were compared with the Zirconium-Hydrogen phase system results determined in this study. The Terminal Solid Solubility (α -Zr) was approximated by the onset precipitation temperature where there is no gradient of stress nor of concentration at the hydride-metal interface in an equilibrated system. Another equilibrium line corresponds to threshold concentrations where hydrides form at local tensile stress risers in the metal. The hydride threshold concentrations on heating agree with previous DHC initiation concentrations on cooling, which suggests no thermal hysteresis.

Declarations

- Work presented in this thesis has not been submitted to any other degree application or institute of learning.
- This thesis is original unless referenced to acknowledge the original author(s).
- Permission to use this work must be obtained from Leigh Corrigall; otherwise, use (including distribution) is a violation of intellectual property.

Acknowledgements

Glenn A. McRae

Scott T. Langille

Curtis St. Louis

Christopher E. Coleman

Stanley Conley

Fraser K. Kirby

Kieran Sutch

Heidi Nordin

Vicky Hilton

Tables of Contents

ABSTRACT	II
DECLARATIONS	III
ACKNOWLEDGEMENTS	IV
1. INTRODUCTION	1
1.1. OBJECTIVES	3
1.2. ORGANISATION	4
2. LITERATURE REVIEW	6
2.1. HYDROGEN IN CANDU REACTOR COMPONENTS	7
2.1.1. <i>Delayed Hydride Cracking</i>	9
2.1.2. <i>Leak-Before-Break Principle</i>	11
2.1.3. <i>Irradiation Damage During Service</i>	12
2.2. ZIRCONIUM-HYDROGEN PHASE SYSTEM	13
2.2.1. <i>The Terminal Solid Solubility (α-Zr)</i>	15
2.2.2. <i>Gamma (γ-ZrH)</i>	17
2.2.3. <i>Delta (δ-ZrH_x)</i>	18
2.2.4. <i>Gamma-to-Delta Phase Transition (γ-δ Transition)</i>	19
3. EXPERIMENTAL	20
3.1. MECHANICAL HYDRIDING	21
3.2. MATERIALS SELECTION	23
3.2.1. <i>Choice of Zirconium Alloy</i>	23
3.2.2. <i>Zirconium Hydride as a Source of Hydrogen</i>	24
3.3. DESIGN CONSIDERATIONS	25
3.3.1. <i>Multiple Test Assemblies</i>	25
3.3.2. <i>Continuous Monitoring</i>	27
3.3.3. <i>Circular Geometry Design</i>	28
3.3.4. <i>Weighing Method of the Initial Zirconium Hydride</i>	29
3.4. DIFFERENTIAL SCANNING CALORIMETRY	30
4. THEORY	36
4.1. HYDROGEN IN COPPER	38
4.1.1. <i>Hydrogen Fugacity</i>	40
4.2. MECHANICAL HYDRIDING PREDICTION MODEL	41
4.2.1. <i>No Hydrides in the Metal</i>	43
4.2.2. <i>Hydride Formation in the Metal</i>	44
4.3. HYDROGEN DIFFUSION IN ZIRCONIUM WITH STRESS	47
4.4. GIBBS PHASE RULE	50
5. RESULTS AND DISCUSSION	52
5.1. INITIAL HYDROGEN IN THE ZIRCONIUM METAL	53
5.2. HYDRIDE STOICHIOMETRY IN THE RESIDUAL HYDRIDE	55
5.3. QUANTIFYING THE SOLUBILITY OF HYDROGEN IN COPPER	56
5.4. MASS-BALANCE COMPARED WITH OBSERVATIONS	59
5.5. ZIRCONIUM-HYDROGEN PHASE SYSTEM	61
5.5.1. <i>Gamma (γ-ZrH) and Delta (δ-ZrH_x) Phase Region</i>	61
5.5.1.1. <i>Gamma-to-Delta Phase Transition</i>	63
5.5.2. <i>Regions where Hydrides form in the Metal</i>	65
5.6. EMCC MODEL COMPARISON	67
5.7. IMPLICATIONS	69
6. CONCLUDING REMARKS	73

REFERENCES	77
APPENDICES	86
A. SAMPLE PREPARATION PROCEDURE	86
B. MATERIALS TESTING PROCEDURE	92
C. ANNEALING PROCEDURE	96
D. ANALYSIS BY DIFFERENTIAL SCANNING CALORIMETRY	97
F. OVERVIEW OF HYDROGEN IN THE SYSTEM	99
G. EXPERIMENTAL OUTLIERS	103
Past Experiments	103
Current Experiments	103
Duration	103
Pressure	103
Copper Grades	104
Sample Preparation	104
E. PEGASUS DSC 404 C RESULTS FROM CURTIS ST. LOUIS THESIS	105
F. MTS 810 TEST SYSTEM & PEGASUS DSC 404 C RESULTS	118

List of Tables

TABLE 1 - CHEMICAL REQUIREMENTS OF ZIRCALOY-2 (UNS R60802) - ZIRCONIUM-TIN ALLOY	23
TABLE 2 - INITIAL HYDROGEN DATA FOR THE AS-RECEIVED ZIRCALOY-2 SHEET MATERIAL	54
TABLE 3 - SUMMARY OF THE OBSERVED RESIDUAL HYDRIDE STOICHIOMETRY AT SET TEMPERATURES	55
TABLE 4 - THE THRESHOLD CONCENTRATION THAT DEFINES HYDROGEN IN SOLUTION AND HYDRIDES	65

List of Figures

FIGURE 1 - YEARLY ENERGY OUTPUT BY FUEL TYPE IN ONTARIO [3]	6
FIGURE 2 - CANDU 6 FUEL CHANNEL ASSEMBLY [7]	7
FIGURE 3 - ILLUSTRATION OF STEPS INVOLVED FOR DHC AT A NOTCH TIP. THE BLUE GRADIENT REPRESENTS A CHEMICAL POTENTIAL GRADIENT AS A RESULT OF A STRESS GRADIENT.	10
FIGURE 4 - A CONTROVERSIAL Zr-H PHASE DIAGRAM ADAPTED FROM KÖNIGSBERGER [21] BY McRAE [20] WITH RED AND BLUE DASHED LINES INDICATING THE GAMMA AND DELTA PHASE BOUNDARIES RESPECTIVELY. THE FIGURE WAS REPRODUCED FOR THIS THESIS.	14
FIGURE 5 - STANDARD INTERPRETATION OF THE TSS PHASE SOLVUS FOR THE Zr-H SYSTEM	15
FIGURE 6 - VARIATION OF THE NEUTRON DIFFRACTION INTENSITIES OF THE GAMMA, AND DELTA PHASES ON HEATING OF A Zr-2.5Nb SPECIMEN FROM THE AS-RECEIVED CONDITION, ADAPTED FROM ROOT [42].	19
FIGURE 7 - AN EXPLODED VIEW OF THE MECHANICALLY-ASSISTED HYDRIDING TEST ASSEMBLY.....	20
FIGURE 8 - ISOMETRIC PROJECTION AND TOP VIEW OF THE EXPERIMENTAL APPARATUS HAVING FOUR SEPARATE TESTING ASSEMBLIES BETWEEN THREE SPACERS. THE TOP VIEW ON THE RIGHT SHOWS THE CAVITY IN THE CENTRE OF THE SPACER WHERE THE THERMOCOUPLE IS THREADED FROM A PORT STARTING AT THE 12 O'CLOCK POSITION.	22
FIGURE 9 - AN EXAMPLE OF A REPRESENTATIVE HEAT FLOW CURVES FOR DSC ANALYSIS	32
FIGURE 10 - EXAMPLE OF DSC HEATING AND COOLING CURVES (JANUARY 23, 2018 - 172.1 MG) ...	35
FIGURE 11 - AN EXAMPLE ISOTHERM USED TO DETERMINE THE STOICHIOMETRY OF THE RESIDUAL HYDRIDE AT A GIVEN TEMPERATURE. A WHITE CIRCLE REPRESENTS A SINGLE EXPERIMENT AT THE EXPERIMENTAL TEMPERATURE. BLACK CIRCLES ARE LINE INTERCEPTS. THE HORIZONTAL INTERCEPT IS THE INSTANCE WHERE A RESIDUAL HYDRIDE APPEARS IN THE METAL AND AS A RESIDUAL HYDRIDE.	45
FIGURE 12 - ISOTHERMS OF RESIDUAL ZIRCONIUM HYDRIDE	55
FIGURE 13 - PREDICTED SOLUBILITIES OF HYDROGEN IN COPPER DETERMINED FROM EXTRAPOLATIONS OF HIGH-TEMPERATURE MEASUREMENTS. ALSO SHOWN IS THE SOLUBILITY DETERMINED BY THE PERMEABILITY DIVIDED BY DIFFUSIVITY [58], AND THE RESULTS OF THIS STUDY.	56
FIGURE 14 - THE DEVIATION OF HYDROGEN SOLUBILITY IN COPPER PREDICTIONS AND THE OBSERVATIONS MADE FROM S = P / D DATABASE [58]. THE YELLOW BAND IS ONE STANDARD ERROR FOR THE SIEVERTS' RELATION DETERMINED IN THIS STUDY, WHICH IS CONSISTENT WITH THE RATIO OF PERMEABILITY AND DIFFUSIVITY, AS INDICATED BY 0 %.	58
FIGURE 15 - MASS-BALANCE PREDICTIONS (EQUATION 20) COMPARED WITH CONCENTRATIONS OF HYDROGEN IN ZIRCALOY-2 SAMPLES CALCULATED FROM DSC TEMPERATURES. BLACK DIAMONDS ARE EXPERIMENTS THAT CONTAIN NO HYDRIDES IN THE METAL, WHICH ARE MAINLY ATTRIBUTED TO ST. LOUIS [49]. WHITE CIRCLES REPRESENT EXPERIMENTS WHERE HYDRIDES HAVE FORMED IN THE METAL, AND A RESIDUAL HYDRIDE POWDER REMAINS.	60
FIGURE 16 - UPDATED DELTA PHASE SOLVUS (δ -ZrH _x) INDICATED BY THE GOLDEN TRIANGLES FOR THE Zr-H SYSTEM. THE K-FACTOR FOR THE EMCC C+ MODEL WAS CALCULATED TO BE 1.80 ± 0.06 . VERTICAL DOTTED LINES DEFINE WHERE STABLE HYDRIDE CONFIGURATIONS EXIST [30].	62
FIGURE 17 - TSSP OS TEMPERATURE MEASURED BY DSC COMPARED WITH HVE-MS CONCENTRATION	63
FIGURE 18 - TSSP OS MEASUREMENTS AS A FUNCTION OF CONCENTRATION EVALUATED BY HVE-MS. YELLOW CIRCLES ARE THE THRESHOLD CONCENTRATIONS IN TABLE 3. OTHER OBSERVATIONS ARE CONDITIONS FOR DHC INITIATION ON COOLING [20].	66
FIGURE 19 - STOICHIOMETRIC RELATIONSHIP AND MASS BALANCE ACCOUNTABILITY AT 200 °C	99
FIGURE 20 - STOICHIOMETRIC RELATIONSHIP AND MASS BALANCE ACCOUNTABILITY AT 250 °C	99
FIGURE 21 - STOICHIOMETRIC RELATIONSHIP AND MASS BALANCE ACCOUNTABILITY AT 280 °C	100
FIGURE 22 - STOICHIOMETRIC RELATIONSHIP AND MASS BALANCE ACCOUNTABILITY AT 300 °C	100
FIGURE 23 - STOICHIOMETRIC RELATIONSHIP AND MASS BALANCE ACCOUNTABILITY AT 350 °C	101
FIGURE 24 - MASS BALANCE ACCOUNTABILITY AT 425 °C AND 450 °C	101
FIGURE 25 - OVERVIEW OF TSS REGION FOR THE Zr-H SYSTEM WITH THE EMCC MODEL	102
FIGURE 26 - MH-1 DSC - 176.0 MG SPECIMEN - TSSD MS 319.3 °C	105
FIGURE 27 - MH-1 DSC - 176.0 MG SPECIMEN - TSSP MS 244.2 °C	105
FIGURE 28 - MH-2 DSC - 176.0 MG SPECIMEN - TSSD MS 329.7 °C	106
FIGURE 29 - MH-2 DSC - 176.0 MG SPECIMEN - TSSP MS 254.1 °C	106
FIGURE 30 - MH-3 DSC - 185.8 MG SPECIMEN - TSSD MS 325.4 °C	107
FIGURE 31 - MH-3 DSC - 185.8 MG SPECIMEN - TSSP MS 251.3 °C	107
FIGURE 32 - CU-LT DSC - 94.5 MG SPECIMEN - TSSD MS 344.0 °C	108

FIGURE 33 - CU-LT DSC - 94.5 MG SPECIMEN - TSSP MS 270.7 °C.....	108
FIGURE 34 - CU-50 DSC - 180.8 MG SPECIMEN - TSSD MS 268.4 °C.....	109
FIGURE 35 - CU-50 DSC - 180.8 MG SPECIMEN - TSSP MS 189.3 °C.....	109
FIGURE 36 - CU-100 DSC - 178.2 MG SPECIMEN - TSSD MS 268.1 °C.....	110
FIGURE 37 - CU-100 DSC - 178.2 MG SPECIMEN - TSSP MS 188.3 °C.....	110
FIGURE 38 - SAT-1 DSC - 119.3 MG SPECIMEN - TSSD MS 498.5 °C.....	111
FIGURE 39 - SAT-1 DSC - 119.3 MG SPECIMEN - TSSP MS 188.3 °C.....	111
FIGURE 40 - SAT-2BOTTOM DSC - 147.1 MG SPECIMEN - TSSD MS 359.4 °C.....	112
FIGURE 41 - SAT-2BOTTOM DSC - 147.1 MG SPECIMEN - TSSP MS 287.1 °C.....	112
FIGURE 42 - SAT-2MIDDLE DSC - 160.9 MG SPECIMEN - TSSD MS 361.9 °C.....	113
FIGURE 43 - SAT-2MIDDLE DSC - 160.9 MG SPECIMEN - TSSP MS 291.0 °C.....	113
FIGURE 44 - SAT-2TOP DSC - 146.0 MG SPECIMEN - TSSD MS 395.6 °C.....	114
FIGURE 45 - SAT-2TOP DSC - 146.0 MG SPECIMEN - TSSP MS 326.5 °C.....	114
FIGURE 46 - SAT-3BOTTOM DSC - 136.8 MG AND 138.2 MG SPECIMENS - TSSD MS 408.3 °C ..	115
FIGURE 47 - SAT-3BOTTOM DSC - 136.8 MG AND 138.2 MG SPECIMENS - TSSP MS 342.1 °C ..	115
FIGURE 48 - SAT-3MIDDLE DSC - 124.2 MG SPECIMEN - TSSD MS 434.2 °C.....	116
FIGURE 49 - SAT-3MIDDLE DSC - 124.2 MG SPECIMEN - TSSP MS 372.7 °C.....	116
FIGURE 50 - SAT-3TOP DSC - 155.0 MG SPECIMEN - TSSD MS 371.3 °C.....	117
FIGURE 51 - SAT-3TOP DSC - 155.0 MG SPECIMEN - TSSP MS 298.5 °C.....	117
FIGURE 52 - JUN 07, 2016 MTS - 189.964 ± 0.014 kN AT 352.5 ± 0.4 °C FOR 8375 MIN..	118
FIGURE 53 - JUN 07, 2016 DSC - 54.9 MG SPECIMEN - TSSD MS 405.1 °C.....	119
FIGURE 54 - JUN 07, 2016 DSC - 54.9 MG SPECIMEN - TSSP MS 341.1 °C.....	119
FIGURE 55 - JUN 07, 2016 DSC - 78.7 MG SPECIMEN - TSSD MS 438.5 °C.....	120
FIGURE 56 - JUN 07, 2016 DSC - 78.7 MG SPECIMEN - TSSP MS 377.6 °C.....	120
FIGURE 57 - JUN 07, 2016 DSC - 46.3 MG SPECIMEN - TSSD MS 450.0 °C.....	121
FIGURE 58 - JUN 07, 2016 DSC - 46.3 MG SPECIMEN - TSSP MS 383.8 °C.....	121
FIGURE 59 - JUL 04, 2016 MTS - 95.554 ± 0.015 kN AT 353.3 ± 7.2 °C FOR 9950 MIN...	122
FIGURE 60 - JUL 13, 2016 MTS - 117.457 ± 0.014 kN AT 435.3 ± 0.4 °C FOR 7130 MIN..	123
FIGURE 61 - JUL 13, 2016 DSC - 38.2 MG AND 75.8 MG SPECIMENS - TSSD MS 425.9 °C ...	124
FIGURE 62 - JUL 13, 2016 DSC - 38.2 MG AND 75.8 MG SPECIMENS - TSSP MS 361.0 °C ...	124
FIGURE 63 - JUL 20, 2016 MTS - 95.934 ± 0.010 kN AT 364.2 ± 0.4 °C FOR 8350 MIN...	125
FIGURE 64 - JUL 20, 2016 DSC - 56.8 MG SPECIMEN - TSSD MS 373.9 °C.....	126
FIGURE 65 - JUL 20, 2016 DSC - 56.8 MG SPECIMEN - TSSP MS 303.4 °C.....	126
FIGURE 66 - JUL 20, 2016 DSC - 44.8 MG SPECIMEN - TSSD MS 382.7 °C.....	127
FIGURE 67 - JUL 20, 2016 DSC - 44.8 MG SPECIMEN - TSSP MS 313.3 °C.....	127
FIGURE 68 - JUL 20, 2016 DSC - 54.8 MG SPECIMEN - TSSD MS 443.4 °C.....	128
FIGURE 69 - JUL 20, 2016 DSC - 54.8 MG SPECIMEN - TSSP MS 380.4 °C.....	128
FIGURE 70 - AUG 02, 2016 MTS - 89.010 ± 0.009 kN AT 350.6 ± 1.7 °C FOR 8520 MIN...	129
FIGURE 71 - AUG 02, 2016 DSC - 100.3 MG SPECIMEN - TSSD MS 422.5 °C.....	130
FIGURE 72 - AUG 02, 2016 DSC - 100.3 MG SPECIMEN - TSSP MS 355.0 °C.....	130
FIGURE 73 - AUG 15, 2016 MTS - 115.009 ± 0.010 kN AT 347.3 ± 5.5 °C FOR 9995 MIN..	131
FIGURE 74 - OCT 06, 2016 MTS - 17.324 ± 0.011 kN AT 336.9 ± 0.3 °C FOR 8575 MIN...	132
FIGURE 75 - OCT 06, 2016 DSC ANALYSIS - 82.6 MG SPECIMEN - TSSD MS 336.6 °C.....	133
FIGURE 76 - OCT 06, 2016 DSC - 82.6 MG SPECIMEN - TSSP MS 261.1 °C.....	133
FIGURE 77 - OCT 06, 2016 DSC - 72.0 MG SPECIMEN - TSSD MS 383.2 °C.....	134
FIGURE 78 - OCT 06, 2016 DSC - 72.0 MG SPECIMEN - TSSP MS 313.7 °C.....	134
FIGURE 79 - OCT 26, 2016 MTS - 17.170 ± 0.009 kN AT 355.7 ± 0.7 °C FOR 8545 MIN...	135
FIGURE 80 - OCT 26, 2016 DSC - 80.9 MG SPECIMEN - TSSD MS 311.6 °C.....	136
FIGURE 81 - OCT 26, 2016 DSC - 80.9 MG SPECIMEN - TSSP MS 233.9 °C.....	136
FIGURE 82 - OCT 26, 2016 DSC - 81.5 MG SPECIMEN - TSSD MS 378.2 °C.....	137
FIGURE 83 - OCT 26, 2016 DSC - 81.5 MG SPECIMEN - TSSP MS 308.4 °C.....	137
FIGURE 84 - JAN 19, 2017 MTS - 54.026 ± 0.011 kN AT 352.6 ± 0.4 °C FOR 8335 MIN...	138
FIGURE 85 - JAN 19, 2017 DSC - 54.2 MG SPECIMEN - TSSD MS 338.8 °C.....	139
FIGURE 86 - JAN 19, 2017 DSC - 54.2 MG SPECIMEN - TSSP MS 264.6 °C.....	139
FIGURE 87 - JAN 19, 2017 DSC - 69.2 MG SPECIMEN - TSSD MS 416.7 °C.....	140
FIGURE 88 - JAN 19, 2017 DSC - 69.2 MG SPECIMEN - TSSP MS 348.9 °C.....	140
FIGURE 89 - JAN 19, 2017 DSC - 76.2 MG SPECIMEN - TSSD MS 468.3 °C.....	141

FIGURE 90	- JAN 19, 2017 DSC - 76.2 MG SPECIMEN - TSSP MS 407.6 °C	141
FIGURE 91	- FEB 02, 2017 MTS - 71.728 ± 0.013 kN AT 355.0 ± 2.0 °C FOR 8555 MIN...	142
FIGURE 92	- FEB 02, 2017 DSC - 81.1 MG SPECIMEN - TSSD MS 375.1 °C	143
FIGURE 93	- FEB 02, 2017 DSC - 81.1 MG SPECIMEN - TSSP MS 305.9 °C	143
FIGURE 94	- FEB 02, 2017 DSC - 82.4 MG SPECIMEN - TSSD MS 382.2 °C	144
FIGURE 95	- FEB 02, 2017 DSC - 82.4 MG SPECIMEN - TSSP MS 311.2 °C	144
FIGURE 96	- FEB 02, 2017 DSC - 76.0 MG SPECIMEN - TSSD MS 426.4 °C	145
FIGURE 97	- FEB 02, 2017 DSC - 76.0 MG SPECIMEN - TSSP MS 361.5 °C	145
FIGURE 98	- FEB 02, 2017 DSC - 90.8 MG SPECIMEN - TSSD MS 515.8 °C	146
FIGURE 99	- FEB 02, 2017 DSC - 90.8 MG SPECIMEN - TSSP MS 454.3 °C	146
FIGURE 100	- FEB 15, 2017 MTS - 18.762 ± 0.008 kN AT 343.1 ± 1.1 °C FOR 1150 MIN..	147
FIGURE 101	- FEB 15, 2017 DSC - 53.5 MG SPECIMEN - TSSD MS 312.3 °C	148
FIGURE 102	- FEB 15, 2017 DSC - 53.5 MG SPECIMEN - TSSP MS 235.5 °C	148
FIGURE 103	- FEB 15, 2017 DSC - 62.0 MG SPECIMEN - TSSD MS 399.1 °C	149
FIGURE 104	- FEB 15, 2017 DSC - 62.0 MG SPECIMEN - TSSP MS 330.6 °C	149
FIGURE 105	- FEB 15, 2017 DSC - 64.0 MG SPECIMEN - TSSD MS 423.7 °C	150
FIGURE 106	- FEB 15, 2017 DSC - 64.0 MG SPECIMEN - TSSP MS 357.6 °C	150
FIGURE 107	- FEB 16, 2017 MTS - 18.431 ± 0.010 kN AT 366.8 ± 1.2 °C FOR 6995 MIN..	151
FIGURE 108	- FEB 16, 2017 DSC - 101.1 MG SPECIMEN - TSSD MS 302.4 °C	152
FIGURE 109	- FEB 16, 2017 DSC - 101.1 MG SPECIMEN - TSSP MS 225.7 °C	152
FIGURE 110	- FEB 16, 2017 DSC - 100.7 MG SPECIMEN - TSSD MS 374.0 °C	153
FIGURE 111	- FEB 16, 2017 DSC - 100.7 MG SPECIMEN - TSSP MS 303.9 °C	153
FIGURE 112	- FEB 16, 2017 DSC - 109.4 MG AND 97.0 MG SPECIMENS - TSSD MS 409.9 °C .	154
FIGURE 113	- FEB 16, 2017 DSC - 109.4 MG AND 97.0 MG SPECIMENS - TSSP MS 342.2 °C .	154
FIGURE 114	- MAR 03, 2017 MTS - 7.652 ± 0.009 kN AT 355.4 ± 3.3 °C FOR 8360 MIN...	155
FIGURE 115	- MAR 03, 2017 DSC - 75.8 MG SPECIMEN - TSSD MS 457.0 °C	156
FIGURE 116	- MAR 03, 2017 DSC - 75.8 MG SPECIMEN - TSSP MS 389.8 °C	156
FIGURE 117	- APR 12, 2017 MTS - 34.802 ± 0.011 kN AT 351.8 ± 3.5 °C FOR 8410 MIN..	157
FIGURE 118	- APR 12, 2017 DSC - 74.3 MG AND 74.9 MG SPECIMENS - TSSD MS 318.6 °C ..	158
FIGURE 119	- APR 12, 2017 DSC - 78.0 MG SPECIMEN - TSSD MS 371.2 °C	159
FIGURE 120	- APR 12, 2017 DSC - 78.0 MG SPECIMEN - TSSP MS 300.4 °C	159
FIGURE 121	- APR 12, 2017 DSC - 84.8 MG SPECIMEN - TSSD MS 377.9 °C	160
FIGURE 122	- APR 12, 2017 DSC - 84.8 MG SPECIMEN - TSSP MS 308.0 °C	160
FIGURE 123	- APR 12, 2017 DSC - 81.7 MG SPECIMEN - TSSD MS 406.4 °C	161
FIGURE 124	- APR 12, 2017 DSC - 81.7 MG SPECIMEN - TSSP MS 338.4 °C	161
FIGURE 125	- MAY 29, 2017 MTS - 3.129 ± 0.114 kN AT 300.7 ± 4.9 °C FOR 1180 MIN...	162
FIGURE 126	- MAY 29, 2017 DSC - 83.2 MG SPECIMEN - TSSD MS 234.4 °C	163
FIGURE 127	- MAY 29, 2017 DSC - 83.2 MG SPECIMEN - TSSP MS 151.0 °C	163
FIGURE 128	- MAY 29, 2017 DSC - 81.6 MG SPECIMEN - TSSD MS 267.8 °C	164
FIGURE 129	- MAY 29, 2017 DSC - 81.6 MG SPECIMEN - TSSP MS 177.9 °C	164
FIGURE 130	- MAY 29, 2017 DSC - 95.2 MG SPECIMEN - TSSD MS 288.9 °C	165
FIGURE 131	- MAY 29, 2017 DSC - 95.2 MG SPECIMEN - TSSP MS 209.4 °C	165
FIGURE 132	- MAY 29, 2017 DSC - 77.8 MG SPECIMEN - TSSD MS 343.3 °C	166
FIGURE 133	- MAY 29, 2017 DSC - 77.8 MG SPECIMEN - TSSP MS 268.8 °C	166
FIGURE 134	- MAY 30, 2017 MTS - 41.042 ± 0.009 kN AT 301.2 ± 4.8 °C FOR 1190 MIN..	167
FIGURE 135	- MAY 30, 2017 DSC - 60.3 MG SPECIMEN - TSSD MS 290.7 °C	168
FIGURE 136	- MAY 30, 2017 DSC - 60.3 MG SPECIMEN - TSSP MS 212.5 °C	168
FIGURE 137	- MAY 30, 2017 DSC - 64.5 MG SPECIMEN - TSSD MS 369.2 °C	169
FIGURE 138	- MAY 30, 2017 DSC - 64.5 MG SPECIMEN - TSSP MS 297.9 °C	169
FIGURE 139	- MAY 30, 2017 DSC - 64.9 MG SPECIMEN - TSSD MS 403.4 °C	170
FIGURE 140	- MAY 30, 2017 DSC - 64.9 MG SPECIMEN - TSSP MS 335.0 °C	170
FIGURE 141	- MAY 30, 2017 DSC - 76.9 MG SPECIMEN - TSSD MS 430.2 °C	171
FIGURE 142	- MAY 30, 2017 DSC - 76.9 MG SPECIMEN - TSSP MS 365.3 °C	171
FIGURE 143	- MAY 31, 2017 MTS - 41.012 ± 0.010 kN AT 348.3 ± 3.9 °C FOR 1190 MIN..	172
FIGURE 144	- MAY 31, 2017 DSC - 57.5 MG SPECIMEN - TSSD MS 305.6 °C	173
FIGURE 145	- MAY 31, 2017 DSC - 57.5 MG SPECIMEN - TSSP MS 229.0 °C	173
FIGURE 146	- MAY 31, 2017 DSC - 52.1 MG SPECIMEN - TSSD MS 386.5 °C	174

FIGURE 147 - MAY 31, 2017 DSC - 52.1 MG SPECIMEN - TSSP MS 317.5 °C	174
FIGURE 148 - MAY 31, 2017 DSC - 66.2 MG SPECIMEN - TSSD MS 393.6 °C	175
FIGURE 149 - MAY 31, 2017 DSC - 66.2 MG SPECIMEN - TSSP MS 326.5 °C	175
FIGURE 150 - MAY 31, 2017 DSC - 65.0 MG SPECIMEN - TSSD MS 436.6 °C	176
FIGURE 151 - MAY 31, 2017 DSC - 65.0 MG SPECIMEN - TSSP MS 371.9 °C	176
FIGURE 152 - JUN 01, 2017 MTS - 34.891 ± 0.009 kN AT 299.4 ± 4.0 °C FOR 1010 MIN..	177
FIGURE 153 - JUN 01, 2017 DSC - 44.5 MG SPECIMEN - TSSD MS 308.2 °C	178
FIGURE 154 - JUN 01, 2017 DSC - 44.5 MG SPECIMEN - TSSP MS 232.0 °C	178
FIGURE 155 - JUN 01, 2017 DSC - 63.0 MG SPECIMEN - TSSD MS 394.0 °C	179
FIGURE 156 - JUN 01, 2017 DSC - 63.0 MG SPECIMEN - TSSP MS 324.8 °C	179
FIGURE 157 - JUN 01, 2017 DSC - 66.0 MG SPECIMEN - TSSD MS 395.8 °C	180
FIGURE 158 - JUN 01, 2017 DSC - 66.0 MG SPECIMEN - TSSP MS 327.9 °C	180
FIGURE 159 - JUN 01, 2017 DSC - 53.0 MG SPECIMEN - TSSD MS 443.3 °C	181
FIGURE 160 - JUN 01, 2017 DSC - 53.0 MG SPECIMEN - TSSP MS 378.2 °C	181
FIGURE 161 - JUN 02, 2017 MTS - 39.841 ± 0.008 kN AT 279.7 ± 5.6 °C FOR 160 MIN...	182
FIGURE 162 - JUN 02, 2017 DSC - 67.9 MG SPECIMEN - TSSD MS 315.3 °C	183
FIGURE 163 - JUN 02, 2017 DSC - 67.9 MG SPECIMEN - TSSP MS 239.2 °C	183
FIGURE 164 - JUN 02, 2017 DSC - 63.9 MG SPECIMEN - TSSD MS 394.2 °C	184
FIGURE 165 - JUN 02, 2017 DSC - 63.9 MG SPECIMEN - TSSP MS 327.7 °C	184
FIGURE 166 - JUN 02, 2017 DSC - 68.9 MG SPECIMEN - TSSD MS 477.2 °C	185
FIGURE 167 - JUN 02, 2017 DSC - 68.9 MG SPECIMEN - TSSP MS 416.3 °C	185
FIGURE 168 - JUN 02, 2017 DSC - 74.2 MG SPECIMEN - TSSD MS 508.1 °C	186
FIGURE 169 - JUN 02, 2017 DSC - 74.2 MG SPECIMEN - TSSP MS 451.4 °C	186
FIGURE 170 - JUN 05, 2017 MTS - 39.883 ± 0.010 kN AT 281.5 ± 4.9 °C FOR 1165 MIN..	187
FIGURE 171 - JUN 05, 2017 DSC - 64.3 MG SPECIMEN - TSSD MS 347.2 °C	188
FIGURE 172 - JUN 05, 2017 DSC - 64.3 MG SPECIMEN - TSSP MS 273.0 °C	188
FIGURE 173 - JUN 05, 2017 DSC - 57.5 MG SPECIMEN - TSSD MS 435.1 °C	189
FIGURE 174 - JUN 05, 2017 DSC - 57.5 MG SPECIMEN - TSSP MS 368.1 °C	189
FIGURE 175 - JUN 05, 2017 DSC - 75.4 MG SPECIMEN - TSSD MS 473.9 °C	190
FIGURE 176 - JUN 05, 2017 DSC - 75.4 MG SPECIMEN - TSSP MS 408.9 °C	190
FIGURE 177 - JUN 05, 2017 DSC - 82.2 MG SPECIMEN - TSSD MS 537.4 °C	191
FIGURE 178 - JUN 05, 2017 DSC - 82.2 MG SPECIMEN - TSSP MS 490.7 °C	191
FIGURE 179 - JUN 06, 2017 MTS - 39.822 ± 0.009 kN AT 281.5 ± 4.5 °C FOR 1310 MIN..	192
FIGURE 180 - JUN 06, 2017 DSC - 101.1 MG (UNANNEALED) AND 127.4 MG SPECIMENS - TSSD MS 328.6 °C.....	193
FIGURE 181 - JUN 06, 2017 DSC - 101.1 MG (UNANNEALED) AND 127.4 MG SPECIMENS - TSSP MS 251.1 °C.....	193
FIGURE 182 - JUN 06, 2017 DSC - 89.3 MG (UNANNEALED) AND 113.2 MG SPECIMENS - TSSD MS 438.6 °C.....	194
FIGURE 183 - JUN 06, 2017 DSC - 89.3 MG (UNANNEALED) AND 113.2 MG SPECIMENS - TSSP MS 373.7 °C.....	194
FIGURE 184 - JUN 12, 2017 MTS - 91.650 ± 0.012 kN AT 283.0 ± 6.5 °C FOR 160 MIN...	195
FIGURE 185 - JUN 12, 2017 DSC - 63.3 MG SPECIMEN - TSSD MS 452.6 °C	196
FIGURE 186 - JUN 12, 2017 DSC - 63.3 MG SPECIMEN - TSSP MS 387.3 °C	196
FIGURE 187 - JUN 12, 2017 DSC - 77.5 MG SPECIMEN - TSSD MS 423.1 °C	197
FIGURE 188 - JUN 12, 2017 DSC - 77.5 MG SPECIMEN - TSSP MS 357.1 °C	197
FIGURE 189 - JUN 12, 2017 DSC - 78.2 MG SPECIMEN - TSSD MS 357.3 °C	198
FIGURE 190 - JUN 12, 2017 DSC - 78.2 MG SPECIMEN - TSSP MS 285.7 °C	198
FIGURE 191 - JUN 12, 2017 DSC - 67.2 MG SPECIMEN - TSSD MS 435.5 °C	199
FIGURE 192 - JUN 12, 2017 DSC - 67.2 MG SPECIMEN - TSSP MS 370.2 °C	199
FIGURE 193 - JUN 13, 2017 MTS - 22.928 ± 0.008 kN AT 281.9 ± 5.9 °C FOR 160 MIN...	200
FIGURE 194 - JUL 12, 2017 MTS - 100.992 ± 0.014 kN AT 300.7 ± 3.7 °C FOR 1445 MIN..	201
FIGURE 195 - JUL 14, 2017 MTS - 26.019 ± 0.013 kN AT 300.7 ± 2.5 °C FOR 4075 MIN..	202
FIGURE 196 - JUL 19, 2017 MTS - 10.999 ± 0.009 kN AT 281.7 ± 2.8 °C FOR 1330 MIN..	203
FIGURE 197 - JUL 31, 2017 MTS - 21.003 ± 0.149 kN AT 280.5 ± 1.8 °C FOR 1370 MIN..	204
FIGURE 198 - AUG 21, 2017 MTS - 40.801 ± 0.010 kN AT 249.9 ± 3.5 °C FOR 1095 MIN..	205
FIGURE 199 - AUG 21, 2017 DSC - 174.6 MG SPECIMEN - TSSD MS 310.4 °C	206

FIGURE 200	-	AUG 21, 2017	DSC	-	174.6 MG SPECIMEN	-	TSSP MS 230.4 °C		206
FIGURE 201	-	AUG 21, 2017	DSC	-	172.1 MG SPECIMEN	-	TSSD MS 375.2 °C		207
FIGURE 202	-	AUG 21, 2017	DSC	-	172.1 MG SPECIMEN	-	TSSP MS 302.6 °C		207
FIGURE 203	-	AUG 21, 2017	DSC	-	176.0 MG SPECIMEN	-	TSSD MS 298.9 °C		208
FIGURE 204	-	AUG 21, 2017	DSC	-	176.0 MG SPECIMEN	-	TSSP MS 218.4 °C		208
FIGURE 205	-	AUG 21, 2017	DSC	-	176.2 MG SPECIMEN	-	TSSD MS 424.8 °C		209
FIGURE 206	-	AUG 21, 2017	DSC	-	176.2 MG SPECIMEN	-	TSSP MS 353.4 °C		209
FIGURE 207	-	AUG 29, 2017	MTS	-	40.843 ± 0.013 kN AT 282.0 ± 5.3 °C	FOR 1205 MIN..			210
FIGURE 208	-	AUG 29, 2017	DSC	-	173.6 MG SPECIMEN	-	TSSD MS 362.8 °C		211
FIGURE 209	-	AUG 29, 2017	DSC	-	173.6 MG SPECIMEN	-	TSSP MS 289.0 °C		211
FIGURE 210	-	AUG 29, 2017	DSC	-	170.1 MG SPECIMEN	-	TSSD MS 382.1 °C		212
FIGURE 211	-	AUG 29, 2017	DSC	-	170.1 MG SPECIMEN	-	TSSP MS 310.5 °C		212
FIGURE 212	-	AUG 29, 2017	DSC	-	177.6 MG SPECIMEN	-	TSSD MS 346.7 °C		213
FIGURE 213	-	AUG 29, 2017	DSC	-	177.6 MG SPECIMEN	-	TSSP MS 271.0 °C		213
FIGURE 214	-	AUG 29, 2017	DSC	-	175.2 MG SPECIMEN	-	TSSD MS 407.3 °C		214
FIGURE 215	-	AUG 29, 2017	DSC	-	175.2 MG SPECIMEN	-	TSSP MS 340.4 °C		214
FIGURE 216	-	AUG 30, 2017	MTS	-	40.826 ± 0.011 kN AT 275.9 ± 0.2 °C	FOR 1200 MIN..			215
FIGURE 217	-	AUG 30, 2017	DSC	-	173.6 MG SPECIMEN	-	TSSD MS 358.4 °C		216
FIGURE 218	-	AUG 30, 2017	DSC	-	173.6 MG SPECIMEN	-	TSSP MS 283.8 °C		216
FIGURE 219	-	AUG 30, 2017	DSC	-	172.3 MG SPECIMEN	-	TSSD MS 374.0 °C		217
FIGURE 220	-	AUG 30, 2017	DSC	-	172.3 MG SPECIMEN	-	TSSP MS 301.4 °C		217
FIGURE 221	-	AUG 30, 2017	DSC	-	179.1 MG SPECIMEN	-	TSSD MS 345.3 °C		218
FIGURE 222	-	AUG 30, 2017	DSC	-	179.1 MG SPECIMEN	-	TSSP MS 270.7 °C		218
FIGURE 223	-	AUG 30, 2017	DSC	-	174.7 MG SPECIMEN	-	TSSD MS 411.9 °C		219
FIGURE 224	-	AUG 30, 2017	DSC	-	174.7 MG SPECIMEN	-	TSSP MS 342.7 °C		219
FIGURE 225	-	SEP 05, 2017	MTS	-	18.836 ± 0.012 kN AT 349.7 ± 4.5 °C	FOR 8380 MIN..			220
FIGURE 226	-	SEP 05, 2017	DSC	-	168.9 MG SPECIMEN	-	TSSD MS 433.9 °C		221
FIGURE 227	-	SEP 05, 2017	DSC	-	168.9 MG SPECIMEN	-	TSSP MS 364.9 °C		221
FIGURE 228	-	SEP 05, 2017	DSC	-	180.6 MG SPECIMEN	-	TSSD MS 353.1 °C		222
FIGURE 229	-	SEP 05, 2017	DSC	-	180.6 MG SPECIMEN	-	TSSP MS 276.8 °C		222
FIGURE 230	-	SEP 05, 2017	DSC	-	178.8 MG SPECIMEN	-	TSSD MS 343.5 °C		223
FIGURE 231	-	SEP 05, 2017	DSC	-	178.8 MG SPECIMEN	-	TSSP MS 267.2 °C		223
FIGURE 232	-	SEP 05, 2017	DSC	-	175.8 MG SPECIMEN	-	TSSD MS 449.4 °C		224
FIGURE 233	-	SEP 05, 2017	DSC	-	175.8 MG SPECIMEN	-	TSSP MS 380.4 °C		224
FIGURE 234	-	SEP 13, 2017	MTS	-	55.864 ± 0.014 kN AT 282.1 ± 5.4 °C	FOR 1195 MIN..			225
FIGURE 235	-	SEP 13, 2017	DSC	-	173.9 MG SPECIMEN	-	TSSD MS 329.6 °C		226
FIGURE 236	-	SEP 13, 2017	DSC	-	173.9 MG SPECIMEN	-	TSSP MS 253.9 °C		226
FIGURE 237	-	SEP 13, 2017	DSC	-	164.7 MG SPECIMEN	-	TSSD MS 381.1 °C		227
FIGURE 238	-	SEP 13, 2017	DSC	-	164.7 MG SPECIMEN	-	TSSP MS 310.9 °C		227
FIGURE 239	-	SEP 13, 2017	DSC	-	175.6 MG SPECIMEN	-	TSSD MS 383.0 °C		228
FIGURE 240	-	SEP 13, 2017	DSC	-	175.6 MG SPECIMEN	-	TSSP MS 312.4 °C		228
FIGURE 241	-	SEP 13, 2017	DSC	-	170.3 MG SPECIMEN	-	TSSD MS 418.1 °C		229
FIGURE 242	-	SEP 13, 2017	DSC	-	170.3 MG SPECIMEN	-	TSSP MS 351.6 °C		229
FIGURE 243	-	DEC 18, 2017	MTS	-	40.796 ± 0.043 kN AT 255.4 ± 4.8 °C	FOR 1210 MIN..			230
FIGURE 244	-	DEC 18, 2017	DSC	-	174.3 MG SPECIMEN	-	TSSD MS 383.9 °C		231
FIGURE 245	-	DEC 18, 2017	DSC	-	174.3 MG SPECIMEN	-	TSSP MS 314.0 °C		231
FIGURE 246	-	DEC 18, 2017	DSC	-	169.6 MG SPECIMEN	-	TSSD MS 347.6 °C		232
FIGURE 247	-	DEC 18, 2017	DSC	-	169.6 MG SPECIMEN	-	TSSP MS 273.1 °C		232
FIGURE 248	-	DEC 18, 2017	DSC	-	176.7 MG SPECIMEN	-	TSSD MS 332.9 °C		233
FIGURE 249	-	DEC 18, 2017	DSC	-	176.7 MG SPECIMEN	-	TSSP MS 260.9 °C		233
FIGURE 250	-	DEC 18, 2017	DSC	-	177.1 MG SPECIMEN	-	TSSD MS 354.1 °C		234
FIGURE 251	-	DEC 18, 2017	DSC	-	177.1 MG SPECIMEN	-	TSSP MS 282.2 °C		234
FIGURE 252	-	DEC 19, 2017	MTS	-	40.794 ± 0.054 kN AT 253.1 ± 3.8 °C	FOR 1190 MIN..			235
FIGURE 253	-	DEC 19, 2017	DSC	-	177.8 MG SPECIMEN	-	TSSD MS 318.2 °C		236
FIGURE 254	-	DEC 19, 2017	DSC	-	177.8 MG SPECIMEN	-	TSSP MS 241.0 °C		236
FIGURE 255	-	DEC 19, 2017	DSC	-	173.9 MG SPECIMEN	-	TSSD MS 352.8 °C		237
FIGURE 256	-	DEC 19, 2017	DSC	-	173.9 MG SPECIMEN	-	TSSP MS 277.9 °C		237

FIGURE 257 - DEC 19, 2017 DSC - 176.2 MG SPECIMEN - TSSD MS 327.6 °C	238
FIGURE 258 - DEC 19, 2017 DSC - 176.2 MG SPECIMEN - TSSP MS 250.8 °C	238
FIGURE 259 - DEC 19, 2017 DSC - 175.4 MG SPECIMEN - TSSD MS 344.3 °C	239
FIGURE 260 - DEC 19, 2017 DSC - 175.4 MG SPECIMEN - TSSP MS 271.0 °C	239
FIGURE 261 - JAN 10, 2018 MTS - 81.600 ± 0.019 kN AT 201.5 ± 4.0 °C FOR 1335 MIN..	240
FIGURE 262 - JAN 10, 2018 DSC - 173.8 MG SPECIMEN - TSSD MS 311.3 °C	241
FIGURE 263 - JAN 10, 2018 DSC - 173.8 MG SPECIMEN - TSSP MS 234.0 °C	241
FIGURE 264 - JAN 10, 2018 DSC - 174.6 MG SPECIMEN - TSSD MS 302.7 °C	242
FIGURE 265 - JAN 10, 2018 DSC - 174.6 MG SPECIMEN - TSSP MS 223.7 °C	242
FIGURE 266 - JAN 10, 2018 DSC - 171.3 MG SPECIMEN - TSSD MS 329.6 °C	243
FIGURE 267 - JAN 10, 2018 DSC - 171.3 MG SPECIMEN - TSSP MS 254.7 °C	243
FIGURE 268 - JAN 10, 2018 DSC - 171.9 MG SPECIMEN - TSSD MS 349.3 °C	244
FIGURE 269 - JAN 10, 2018 DSC - 171.9 MG SPECIMEN - TSSP MS 272.7 °C	244
FIGURE 270 - JAN 23, 2018 MTS - 142.799 ± 0.033 kN AT 204.2 ± 4.6 °C FOR 1335 MIN..	245
FIGURE 271 - JAN 23, 2018 DSC - 173.0 MG SPECIMEN - TSSD MS 268.8 °C	246
FIGURE 272 - JAN 23, 2018 DSC - 173.0 MG SPECIMEN - TSSP MS 176.3 °C	246
FIGURE 273 - JAN 23, 2018 DSC - 173.4 MG SPECIMEN - TSSD MS 268.9 °C	247
FIGURE 274 - JAN 23, 2018 DSC - 173.4 MG SPECIMEN - TSSP MS 177.3 °C	247
FIGURE 275 - JAN 23, 2018 DSC - 172.3 MG SPECIMEN - TSSD MS 270.0 °C	248
FIGURE 276 - JAN 23, 2018 DSC - 172.3 MG SPECIMEN - TSSP MS 186.6 °C	248
FIGURE 277 - JAN 23, 2018 DSC - 248.7 MG SPECIMEN - TSSD MS 283.7 °C	249
FIGURE 278 - JAN 23, 2018 DSC - 248.7 MG SPECIMEN - TSSP MS 214.3 °C	249
FIGURE 279 - JAN 23, 2018 DSC - 170.3 MG SPECIMEN - TSSD MS 291.3 °C	250
FIGURE 280 - JAN 23, 2018 DSC - 170.3 MG SPECIMEN - TSSP MS 210.7 °C	250
FIGURE 281 - JAN 23, 2018 DSC - 172.1 MG SPECIMEN - TSSD MS 336.4 °C	251
FIGURE 282 - JAN 23, 2018 DSC - 172.1 MG SPECIMEN - TSSP MS 263.9 °C	251

List of Acronyms

CANDU	Canada Deuterium Uranium (reactor)
CNL	Canadian Nuclear Laboratories
CNSC	Canadian Nuclear Safety Commission
CSA	Canadian Standards Association
CT	Calandria Tube
CT	Completion Temperature of TSSD or TSSP
DEM	Dynamic Elastic Modulus
DFM	Diffusion First Model
DHC	Delayed Hydride Cracking
DSC	Differential Scanning Calorimetry
EMCC	Einstein-McRae-Coleman-Cottrell model
HCP	Hexagonal Close-Packed
HSM	Hot Stage Microscopy
HVE-MS	Hot-Vacuum-Extraction Mass-Spectroscopy
HWR	Heavy Water Reactors
IESO	Independent Electricity System Operator
LBB	Leak-Before-Break
LOCA	Loss-of-Coolant Accident
FFSG	Fitness-for-Service Guidelines
MS	Maximum Slope temperature of TSSD or TSSP
MTS	Materials Testing Machine
OEB	Ontario Energy Board
OS	Onset temperature of TSSP
PT	Peak Temperature of TSSD
PT	Pressure Tube
TCU	Thermal Control Unit
TSS	Terminal Solid Solubility
TSSD	Terminal Solid Solubility Dissolution
TSSP	Terminal Solid Solubility Precipitation
UTS	Ultimate Tensile Strength or Ultimate Yield Strength
XRD	X-Ray Diffraction

1. Introduction

Zirconium alloys are used in the core of nuclear reactors because of their low neutron capture cross-sections, mechanical strength, and corrosion resistance. The corrosion of zirconium alloys leads to the ingress of a small amount of hydrogen, which changes material properties. Hydrogen embrittles the metal and lowers ductility and fracture toughness. Furthermore, hydrogen can move to regions of tensile stress associated with flaws that can lead to failures of pressure boundaries in the core by a mechanism called Delayed Hydride Cracking (DHC).

Currently, there are financial incentives in the nuclear industry to extend the service life of reactors beyond their original design. Engineers are being asked to justify future Fitness-for-Service Guidelines (FFSG). Extrapolations of future FFSG will require a thorough understanding of hydrogen phases in zirconium.

Current FFSG include empirically based engineering equations with large safety margins. These equations work for daily operation, but they cannot be extrapolated unless they are consistent with scientific principles. An added benefit of a sound physical model is that the safety margins might be reduced, which could reduce maintenance costs.

The Zr-H phase diagram has been the subject of much speculation and debate over the last 60 years [1]. For instance, multiple solvi are used to describe the Terminal Solid Solubility (TSS) (α -Zr) of hydrogen in zirconium, and multiple independent hydride phases are believed to exist simultaneously in equilibrium with hydrogen in zirconium, which is apparently inconsistent with Gibbs' Phase Rule - the foundation of all phase equilibrium diagrams.

Part of the process to develop a physical model is testing predictions against interpretations of experimental observation. Methods are being developed to add hydrogen quantitatively to approximate end-of-life conditions in reactor components as part of ongoing model validation. In particular, methods are sought that will not compromise other end-of-life characteristics, such as irradiation damage.

1.1. Objectives

- i. Develop a method to add hydrogen quantitatively to zirconium alloys that can be used to approximate reactor end-of-life conditions of hydrogen concentrations and irradiation damage
- ii. Map the Zr-H phase diagram in the range of reactor operating temperatures, specifically:
 - o α -Zr, the Terminal Solid Solubility (TSS)
 - o γ -ZrH (could the phase be meta-stable?)
 - o δ -ZrH_x
 - o ε -ZrH₂
- iii. Test predictions of the Einstein-McRae-Coleman-Cottrell (EMCC) model

1.2. Organisation

The thesis is grouped into six sections, beginning with the *Introduction* (Section 1), *Objectives* (Section 1.1) and *Organisation* (Section 1.2)

The *Literature Review* (Section 2) introduces aspects of Hydrogen in CANDU Reactor Components (Section 2.1) that depend on the *Zirconium-Hydrogen Phase System* (Section 2.2). To study Delayed Hydride Cracking of irradiated zirconium alloys, hydrogen must be added without annealing irradiation damage.

The *Experimental* (Section 3) section introduces *Mechanical Hydridding* (Section 3.1) followed by the *Material Selection* (Section 3.2) and *Design Considerations* (Section 3.3). In the same section, a technique for measuring heat flow as a function of a temperature associated with hydrogen concentration in zirconium called *Differential Scanning Calorimetry* (Section 3.4) is discussed beginning with conventional interpretations.

The *Theory* (Section 4) section provides an outline of how the mass-balance equation is used to account for hydrogen in the experimental test assembly. This section includes a solubility model of *Hydrogen in Copper* (Section 4.1) that depends on *Hydrogen Fugacity* (Section 4.1.1) followed by the *Mechanical Hydriding Prediction Model* (Section 4.2) that considers two cases: when *No Hydrides in the Metal* (Section 4.2.1) exist, and when *Hydride Formation in the Metal* (Section 4.2.2) does occur. The *Theory* section finishes with the *Hydrogen Diffusion in Zirconium with Stress* (Section 4.3) under a no-flux condition where Gibbs Phase Rule (Section 4.4) applies.

Results and Discussion (Section 5) are presented, ending with *Implications* (Section 5.7). The *Conclusions* (Section 6) discuss the results of the study in terms of its original *Objectives* (Section 1.1).

Appendices include *Sample Preparation* (Appendix A), *Materials Testing* (Appendix B), *Annealing* (Appendix C), and *Analysis by Differential Scanning Calorimetry* (Appendix D). These detailed procedures explain how the experimentation is performed. *Experimental Outliers* are found in Appendix G with some examples. Information collected during experimentation and Differential Scanning Calorimetry results are presented in Appendix E to F.

2. Literature Review

Canada's nuclear energy fleet consists of CANDU reactors. In Ontario, 63 % of electricity comes from operating nuclear power plants (Figure 1). CANDU reactors have a reputation for safe and reliable operation. Safety is ensured by operation within strict Fitness-for-Service Guidelines (FFSG) managed by the Canadian Standards Association (CSA) and regulated by the Canadian Nuclear Safety Commission (CNSC) [2].

Figure 1 - Yearly energy output by fuel type in Ontario [3]

CSA Standard 285.8 prescribes FFSG requirements for the fuel channels in the core of the reactor [4]. The goal of the Standard is to prevent pressure boundary failures. In the unlikely event of a failure, the reactor could be disabled for months, if not years, and may not return to service depending on the severity. Based on the current cost of energy [5], lost revenue could be in the range of ten million dollars daily, in addition to the cost of replacement power, repair, etc.

2.1. Hydrogen in CANDU Reactor Components

Canada Deuterium Uranium (CANDU) reactors are Heavy Water Reactors (HWR) which pressurise the heat transport system where coolant flows inside pressure tubes between the fuel bundles (Figure 2). A pressure tube rests inside a calandria tube where annulus gas insulates the heat transport fluid from the moderator and provides a path for decay heat in the event of a Loss-of-Coolant Accident (LOCA) [6]. The annulus gas, between the pressure tube and the calandria tube, is monitored to defend Leak-Before-Break (LBB) discussed in Section 2.1.2. A CANDU reactor consists of hundreds of fuel channel assemblies.

Figure 2 - CANDU 6 Fuel Channel Assembly [7].

During service, CANDU pressure tubes operate at temperatures between 250 °C and 310 °C, with coolant pressures up to 11.3 MPa, which produces hoop stress that can provide the tensile stress to promote axial Delayed Hydride Cracking (DHC) (Section 2.1.1). The pressure tubing is also subjected to fast neutrons produced from fission of the fuel for up to 30 years during service life. Pressure tubes are embrittled because of deuterium ingress during service. A pressure tube will absorb some of the deuterium produced by aqueous corrosion:

Equation 1

Also, hydrogen diffuses into the pressure tube from the stainless-steel end fitting. If the concentration of hydrogen is sufficient, hydrides can nucleate. The concentration of hydrogen in solution, adjacent to the hydride, is the Terminal Solid Solubility (TSS) (α -Zr) concentration.

CANDU pressure tubes are regularly inspected as prescribed by FFSG. Scrape samples (approximately 10 cm long, 1 cm width, 200 μm depth) are taken from the inside surface of the tube for hydrogen analysis with Hot-Vacuum-Extraction Mass-Spectroscopy (HVE-MS). Routine inspection ensures FFSG have been met by the operator.

2.1.1. Delayed Hydride Cracking

A time-dependent mechanism called DHC in zirconium has received considerable attention because of the direct impact this phenomenon has on CANDU reactors. This crack growth mechanism has led to failures in Zr-2.5Nb fuel cladding [8] and pressure tubes [9], among other materials [10] [11] [12].

The basic steps used to describe DHC (Figure 3):

- 1) Nucleation of a hydride at a stress-raiser: Hydrogen diffuses along a chemical potential gradient ($\nabla\mu$) as a consequence of stress gradient ($\nabla\sigma$).
- 2) The growth of the hydride: A hydride will form when precipitation is preferred over a solubility in solid solution.
- 3) Conditions for fracture are satisfied: A minimum threshold condition for stressing, usually characterised by a stress intensity factor (K_{IH}), must be exceeded before cracking initiates. Once initiated, crack growth becomes independent of the stress intensity factor (K_I).

Repetition of these steps leads to stable crack growth rates.

Figure 3 - Illustration of steps involved for DHC at a notch tip. The blue gradient represents a chemical potential gradient as a result of a stress gradient.

Crack growth rate depends on temperature, thermal history, and irradiation. DHC is diffusion limited: crack growth rate is controlled by the rate of hydrogen arrival to the region of the crack tip.

DHC limits the amount of hydrogen, stress, and thermal history permitted in pressure tubes during operation [13]. Conservatively remaining within these limitations permits the safe operation of a reactor. Better understanding of failure mechanisms could reduce uncertainties of end-of-life prediction.

2.1.2. Leak-Before-Break Principle

CANDU reactors use Leak-Before-Break (LBB) to demonstrate that DHC can be controlled. The principle of LBB is that the failure can be detected during leaking before catastrophic failure on breaking [14]. Heavy water enters the annulus gas system from the heat transport side and flashes to steam when a DHC in the pressure tube penetrates its outer diameter. A leak is detected on a chilled mirror by monitoring the dew point and its rate of increase. This process requires time for the heavy water vapour to reach the detection system [15]. To defend LBB, the DHC growth rate must be slow enough that the crack is detectable before it becomes unstable and that the crack is less than a critical length.

The probability that a LBB is detected decreases during service [16]; irradiation increases the yield strength of the zirconium alloy, which increases DHC growth rate. DHC models are validated with irradiated pressure tube material to which end-of-life hydrogen concentrations have been added without removing the irradiation damage. Additionally, the DFM for DHC is based on the same formalism as the EMCC model that will be used to describe the Zr-H phase diagram in this thesis.

2.1.3. Irradiation Damage During Service

In regular service, fast neutrons in the core of the reactor cause dislocations that increase the tensile strength of the zirconium matrix by impeding movement along slip planes. DHC growth rates are faster for high-strength materials. Another concern with irradiation damage is that it may affect hydride precipitation and dissolution processes through trapping [17].

Furthermore, the effect of 1-hour annealing at 300 °C modifies the Ultimate Tensile Strength (UTS) of cold-worked Zr-2.5Nb irradiated pressure tubing tested at room temperature (P3-F13) or 300 °C (P4-N16) by less than 5 % [18]. To simulate end-of-life behaviour, hydrogen must be quantitatively added to irradiated zirconium alloys without changing fracture properties. Thus, hydrogen addition must be completed rapidly at temperatures below 300 °C to avoid modifying the irradiation effects on zirconium alloys.

2.2. Zirconium-Hydrogen Phase System

According to Sieverts [19], Clemens A. Winkler may have been the first to discover epsilon hydride (ϵ -ZrH₂) prior to World War II. Much debate exists around the current Zr-H phase system¹. Currently, there are three accepted crystallographic phases of zirconium hydride: gamma (γ -ZrH), delta (δ -ZrH_x), and epsilon (ϵ -ZrH₂). Figure 4 illustrates a recently published interpretation of the Zr-H phase system with measurements for the Terminal Solid Solubility (TSS) (α -Zr) and delta solvus (δ -ZrH_x).

Sections 2.2.1, 2.2.2, 2.2.3, and 2.2.4 outline basic research on phase boundaries within the scope of this. Additional background can be accessed through McRae [20], which covers a detailed overview of gamma (γ -ZrH) and delta (δ -ZrH_x) hydrides in zirconium.

¹ [19] [41] [23] [113] [24] [25] [112] [33] [37] [114] [29] [35] [28] [111] [97] [110] [98] [99] [21] [1] [109] [108] [20]

Figure 4 - A controversial Zr-H phase diagram adapted from Königsberger [21] by McRae [20] with red and blue dashed lines indicating the gamma and delta phase boundaries respectively. The figure was reproduced for this thesis.

2.2.1. The Terminal Solid Solubility (α -Zr)

Since Erickson [22], and others [23] [24] [25], recognised differences attributed to hydride precipitation and dissolution by dilatometry of the TSS, there has been a common acceptance that a hysteresis is present in zirconium alloys in the nuclear industry. In the standard interpretation of the TSS, both lines represent equilibrium conditions (Figure 5) depending on heating (Dissolution, **TSSD**) or cooling (Precipitation, **TSSP**).

Figure 5 - Standard interpretation of the TSS phase solvus for the Zr-H System

Using Figure 5 as an example, the cooling-heating cycle begins at **A** (75 ppm, 350 °C) where all the hydrogen is in solution. As the zirconium material is cooled, the hydrogen concentration in solution remains constant until reaching **B**. At this temperature and concentration, there is no observable effect by crossing the dissolution solvus (**TSSD**). On further cooling, hydrides nucleate below 253 °C. As hydrides form, the concentration of hydrogen in solution follows the precipitation solvus as the material cools to **C**. In the heating portion of the cycle, the material is heated on reaching **C** until **D**. During the heating process, there is no observable impact made by crossing the precipitation solvus (**TSSP**), and the concentration (50 ppm) remains the same. There is, however, an impact made by reaching the dissolution solvus at **D**. On heating above 291 °C, the solvus is given by the dissolution solvus (**TSSD**) where hydrides begin to dissolve until **E**. At this point, the concentration becomes 75 ppm again. When heated further, from **E** to **A**, the concentration remains constant.

According to McRae [20] there is a single TSS for zirconium which complies with Gibbs Phase Rule [26] for one degree-of-freedom: for a two-component system, only two phases can exist at equilibrium under isobaric and isothermal conditions.

2.2.2. Gamma (γ -ZrH)

Gamma phase hydrides (γ -ZrH) have been reported to be metastable [27], like martensite in steels, in spite of evidence showing that the 'amount of gamma in solid samples is difficult to alter' [28]. Douglas [29] was the first to suggest that the gamma phase is stable by presenting Gulbrandsens' experimental data [23] on the phase diagram. More recently, claims of a stable gamma hydride have been made [30] and the gamma phase boundary has been included in some phase diagrams [31] [32] [20]. Gamma hydrides exist, although it remains controversial whether the phase is stable.

2.2.3. Delta (δ -ZrH_x)

The delta phase solvus (δ -ZrH_x) for the zirconium-hydrogen system [21] is a product of XRD [33], dilatometry and Hot Stage Microscopy (HSM) [28], and diffusion-couple methods [34]. The phase boundary, in general, is incomplete and often relies on single experimental observations; hence it is vulnerable to uncertainty. What is more concerning is that some information from Königsberger [21] is missing [28] [35] [36] [37] [38] [39] [40] [24] [41], which indicates that the phase diagram is interpreted.

2.2.4. Gamma-to-Delta Phase Transition (γ - δ Transition)

Experiments by Root [42] and others [43] [44] claim to have identified the gamma-to-delta phase transition. Root suggests the transformation occurs at 187 ± 10 °C, on heating Zr-2.5Nb at a rate of 2.5 °C per minute when changing set temperatures (Figure 6). The majority of Zr-H phase diagrams do not possess this transition line. Transformations nearing 200 °C occur in the titanium-hydrogen system [45] that are similar to the Zr-H phase system.

Although the gamma phase (γ -ZrH) remains relatively constant after transformation in Figure 6, the delta phase (δ -ZrH_x) appears to descend at higher temperatures gradually. Another drastic change occurs at 282.3 ± 5.2 °C where both hydrides dissolve.

Figure 6 - Variation of the neutron diffraction intensities of the gamma, and delta phases on heating of a Zr-2.5Nb specimen from the as-received condition, adapted from Root [42].

3. Experimental

The objective was to add hydrogen into zirconium without altering irradiation properties (Objective i). The test assembly is represented schematically in Figure 7. The system consists of two copper plates, a zirconium disc, and zirconium hydride powder. The powder is distributed on the disc, which is placed between the plates. Test assemblies are compressed from 11 MPa to 320 MPa, heated to a target temperature in the range of 200 °C to 450 °C, for times between 3 hours and 167 hours. The details of the procedure are discussed in Appendices A through D. The rationale for the experimental design is presented below.

Figure 7 - An exploded view of the mechanically-assisted hydriding test assembly

3.1. Mechanical Hydriding

If the objective is to add hydrogen to metal, then many metallic hydrides can be used as long as they decompose at a reasonable temperature, are safe to use, and the hydride decomposition products do not adversely react with the metal. However, in this thesis, the objective is to map the Zr-H phase diagram (Objective ii), which is a two-component system. No other components can be introduced, which means only zirconium hydrides can be used as a hydrogen source.

The copper plates provide a hydrogen barrier, which establishes a foundation for a mass-balance equation that makes the mechanically-assisted hydrogen addition technique quantitative. The oxide layer on the external copper surfaces of the test assembly is sufficient to prevent hydrogen egress [46].

The compressive yield strength of copper is less than that of zirconium. When the external pressure applied, the copper deforms around the zirconium and hydride powder -- forming a seal that prevents hydrogen gas from escaping during a test.

Without outside oxygen to replenish the oxides inside the sealed test assembly, the oxides on the metals become unstable as the oxygen diffuses into the zirconium. The reducing environment at the copper-zirconium interface degrades surface oxides, rendering them no longer effective hydrogen barriers. When hydrogen is liberated by the thermal decomposition of the zirconium hydride, it can move into the metals. The negative hydrostatic stress, equivalent to the hydrogen pressure, is calculated from the force applied and the total contact area of each assembly. Figure 8 illustrates four test assemblies before compression.

Figure 8 - Isometric projection and top view of the experimental apparatus having four separate testing assemblies between three spacers. The top view on the right shows the cavity in the centre of the spacer where the thermocouple is threaded from a port starting at the 12 o'clock position.

Test assemblies are arranged symmetrically to distribute load evenly across the plates. Two thermocouples are placed in the central cavity and connected to acquisition and control through radial ports.

3.2. Materials Selection

3.2.1. Choice of Zirconium Alloy

Zircaloy-2 is predominantly alpha phase (α -Zr) Hexagonal Close-Packed (HCP) zirconium, which is desirable for studying the binary Zr-H phase diagram. Hydrogen solubility of the pure metal is similar to that of Zircaloy-2 [34]. The composition is listed in Table 1 [47]. Zircaloy-2 has been developed and extensively studied for nuclear applications.

Composition, Weight %																	
Sn	Fe	Cr	Ni	Nb	O	Fe + Cr + Ni	Fe + Cr										
1.20-1.70	0.07-0.20	0.05-0.15	0.03-0.08	∴	*	0.18-0.38	∴										
Maximum Impurities, Weight %																	
C	Si	W	Hf	Nb	H	Co	Mg	N	Al	Cu	Mn	Mo	Ti	Ca	U	B	Cd
0.027	0.0120	0.010	0.010	0.0100	0.0025	0.0020	0.0020	0.0080	0.0075	0.0050	0.0050	0.0050	0.0050	0.0030	0.00035	0.00005	0.00005

* When specified in the purchase order, oxygen shall be determined and reported. Maximum, minimum, or both, permissible values should be specified in the purchase.

Table 1 - Chemical requirements of Zircaloy-2 (UNS R60802) - zirconium-tin alloy

3.2.2. Zirconium Hydride as a Source of Hydrogen

Zirconium(II) hydride powder or epsilon phase hydride (ϵ -ZrH₂) was purchased from Sigma-Aldrich Canada [48]. Zirconium hydride is stable at room temperature, making it safe to handle. The hydride is made precisely by pulverising pure zirconium and reacting it with hydrogen at high temperatures. According to Sigma-Aldrich, gravimetric analysis reveals that the powder contains 96.4 – 99.3 % by weight of zirconium on ignition to oxide. This amounts to a mass fraction:

$$F = (0.0212 \pm 0.0002) \frac{\text{g H}}{\text{g ZrH}_2}$$

Equation 2

Zirconium hydride decomposes to form hydrogen gas on heating which is absorbed into the zirconium and copper as monatomic hydrogen. The accuracy of the added amount of hydrogen is based on the accuracy of the analytical balance used to measure the zirconium hydride.

3.3. Design Considerations

Significant modifications were made to the original experimental design of St. Louis [49] to improve measurement accuracy and performance so that the work could be done as efficiently as possible within a thesis timeframe. Initially, experiments took up to 5 days to add hydrogen to a zirconium sample [49].

3.3.1. Multiple Test Assemblies

The previous design incorporated vertical stacking of test assemblies to enable multiple experiments to run simultaneously under similar conditions. However, there were negative consequences of this design because they become misaligned, which compromises the seals and allows hydrogen to escape.

Another issue associated with vertically stacked testing assemblies is that the thermal profile of the oven can vary by tens of degrees over a stacking distance of a few centimetres. Stacking increases the uncertainty of the test temperature and limits the experiments to three vertically stacked test assemblies, separated by two hardened steel cylindrical spacers (2-inch diameter by 1.6-inch length).

In this thesis, single stacks were utilised to avoid the issues associated with vertical stacking. Typically, 3 to 7 test assemblies were arranged on the same plane in the oven (Figure 8). The advantage of this configuration is that all test assemblies share the same experimental conditions of pressure and temperature, which made outliers easier to distinguish when systematically varying the zirconium hydride powder added.

The single stack setup (Figure 8), with multiple test assemblies, increased the rate at which experiments could be done when compared to a single test assembly setup. This was accomplished by reducing the size of the test assemblies.

3.3.2. Continuous Monitoring

The Materials Testing Machine (MTS) computer software was updated to record displacement and applied force of the tensile testing machine. An EL-USB-TC-LCD USB Thermocouple Data Logger was used to record sample temperature and to determine the duration of each trial accurately by measuring the difference of time between when the target temperature was initially reached and when the quenching process began.

The hardened steel spacers were arranged to accommodate two thermocouples positioned at the testing plane. Positioning the thermocouples together ensured that the Thermal Control Unit (TCU) made adjustments on behalf of the samples, rather than for a region of the oven and that the data logger was recording these test assembly temperatures accurately. Continuous sample monitoring with the data logger did more than improving experimental accuracy. Without this battery-operated feature, failed experiments caused by power interruptions and other interferences may not have been identified. Continuous monitoring contributed to the discovery of rapid hydrogen addition at low temperatures; hydrogen can be added to zirconium in as little as 20 hours at 200 °C.

3.3.3. Circular Geometry Design

The precision of disc manufacturing was important for the experimental design because the applied stress was calculated based on geometric area. The sensitivity of hydrogen solubility in copper or zirconium on applied stress at the beginnings of this research project was unknown. Initially, the zirconium discs were square, but this geometry complicated simple stress analysis calculations. In this thesis, circular discs were used because they were simple to produce precisely with a standard punch, and because there are no corners, the stress calculation was better defined, even with some deformation of the copper. Eliminating the corners also meant that more test assemblies could be fitted onto a spacer set on the MTS. This improvement made it possible to run as many as 7 test assemblies simultaneously.

3.3.4. Weighing Method of the Initial Zirconium Hydride

Preparation instructions from Appendix A outline a method for weighing materials accurately in order to reduce measurement error. Each test assembly was prepared individually on an analytical balance (Acculab ALC-210.4) to ensure there was sufficient mass on the weighing platform to be within acceptable measuring tolerance [50]. No beakers or paper sheets were used to transfer the powder. The mass of metal plates was measured twice: once as part of the procedure to estimate a target concentration for zirconium hydride; and again prior to the addition of zirconium hydride to verify the first measurement. This method reduced the loss of zirconium hydride powder during experimental setup and was important for measuring masses as low as 1.1 mg. The method consisted of measuring the copper plates together, then combining them with the zirconium disc, and then a final measurement was made of the zirconium hydride powder before the top copper plate was placed on the rest of the test assembly (see Figure 7).

3.4. Differential Scanning Calorimetry

Attempts are still being made to measure the TSS of the Zr-H system. These techniques may include partitioning of hydrogen in diffusion-couples, acoustic emission during DHC, measurement of the Dynamic Elastic Modulus (DEM), dilatometry [22], and Differential Scanning Calorimetry (DSC) [51]. All require some level of interpretation to relate the measured signal to the TSS [42].

DSC are analytical instruments used to measure phase transitions in materials. The DSC 404 F1 Pegasus® system chosen for this study operates according to the heat flux principle: the actual measured properties are the temperature of the sample, which contains hydrogen, and the temperature difference between sample and reference during heating and cooling continuously with a controlled temperature program. From the raw signals, the heat flow difference between sample and reference² can be determined [52].

² The DSC reference is an important aspect of the results. See Section 5.1.

The difference in heat flow is attributed to dissolution or precipitation of hydrides. The temperature dependence of the heat flow curves changes with different amounts of hydrogen in the metal, which can be calibrated with concentrations of hydrogen determined by HVE-MS. These calibration curves have been used to report temperatures and concentrations as low as 100 °C and 5 ppm for hydrogen in zirconium [17].

The DSC technique was selected because it was readily available, based on simple physical principles, and provides excellent reproducibility at low costs. The analysis is considered to be non-destructive which allows specimens to be repeatedly measured.

Before DSC analysis, a number of calibrations were performed using metal standards with known melting points. This requirement allows for a high degree of measurement certainty within the range of the standards used. A thermal lag correction was applied to the temperature measurements to compensate for the sample mass (that varied between 43.1 and 195.2 mg) and a heating rate of 10 °C per minute. The correction was provided by the Canadian Nuclear Laboratories (CNL) in the form of an Excel Spreadsheet [53].

The equation based on a regression model is provided below:

$$T_f(^{\circ}\text{C}) = T_i(^{\circ}\text{C}) - 0.000353 \frac{\text{min}}{\text{mg}} * \left[\left(m_{\text{sample}} * 10 \frac{^{\circ}\text{C}}{\text{min}} \right) - \left(85 \text{ mg} * 10 \frac{^{\circ}\text{C}}{\text{min}} \right) \right]$$

Equation 3

For the DSC Pegasus® system, measurement repeatability is in the range of 0.1 °C to 0.4 °C between 150 °C and 700 °C, depending on the melting temperature of the specimens and the type of crucible used [54]. As a general rule, the higher the temperature, the greater the uncertainty.

Figure 9 illustrates typical DSC heating and cooling heat flow curves used to estimate **TSS Dissolution** (TSSD) and **TSS Precipitation** (TSSP) temperatures. The heat flow curves are often described with distinctive temperatures.

Figure 9 - An example of a representative heat flow curves for DSC analysis

For **TSSD**, the features shown in Figure 9 are:

B. Peak Temperature (PT) represents the maximum deviation of the heat flow along a perpendicular to the interpolated baseline of the heat flow curve.

C. Maximum Slope (MS) temperature is where the absolute value of the derivative of heat flow curve, represented as a **red dotted line**, is a local maximum. In Figure 9, this temperature is associated with a minimum value of the heat flow, but regardless the temperature is referred to a "maximum". The MS temperature is often used because it is insensitive to linear backgrounds in the heat flow. The MS conventionally defines TSSD.

D. Completion Temperature (CT) is the temperature at which the interpolated baseline and the average dissolution discontinuity tangent intersect [17]. The CT is interpreted as the temperature where all hydrides have completely dissolved.

The **solid blue line** represents the heat flow curve on cooling in Figure 9; the features are similar to the heating curve except inverted. The distinct temperatures on cooling are:

E. Onset (OS) temperature is the intersection of the tangents of the MS with the extrapolated baseline. This is the temperature where a thermal signal from hydride precipitation is first observed on cooling from a temperature where all the hydrogen was in solution.

F. Maximum Slope (MS) temperature defines TSSP from the derivative as defined for the heating curve (for TSSD MS: point C and for TSSP MS: point F).

A concentration of hydrogen in Zircaloy-2 is measured directly by HVE-MS in units of ppm by weight [17] and is related to the MS temperature of the TSSD measured using DSC by the following relation above 170 °C:

$$C_{H \text{ in } Zr}[\text{ppm}] = 106\,446.7 \cdot \exp\left(-\frac{4328.67}{T_{TSSD \text{ MS}}[\text{K}]}\right)$$

Equation 4

Although it is often referred to as such, Equation 4 is not an equilibrium solvus.

An example of the predefined temperature pathway is shown in Figure 10 which has three heating and cooling cycles between 200 °C and 550 °C. The first heating run and the last cooling run were used to measure the MS temperatures of the reference (seen in Figure 9 as A. and H.). Heat flow curves peak in the opposite direction for the reference because the measurement is based on a difference.

Figure 10 - Example of DSC heating and cooling curves (January 23, 2018 - 172.1 mg)

The TSSD and TSSP temperatures of the as-received Zircaloy-2 references were measured for each sample analysis, which enabled high-precision measurements.

4. Theory

Conservation of mass is commonly applied to closed systems having a single degree-of-freedom. By comparison, the solvus lines of a binary phase diagram can be mapped when there is a single degree-of-freedom. The objective of the thesis is to gain an understanding of the physical system where an equilibrium takes place between the zirconium, copper, and hydrogen. This understanding is in the form of a prediction model (Objective i) and a thermodynamic model (Objective iii) based on first principles.

In this scenario, copper is not a hydride forming metal. Its purpose is to secure a barrier so that hydrogen cannot escape to the surroundings. Thus, maintaining conservation of mass. Although copper absorbs a fraction of the total hydrogen in the system at equilibrium, this amount is known from Sievert's law (Section 4.1).

The hydrogen trapped inside the system can form a phase equilibrium at elevated temperatures with zirconium. The amount of hydrogen absorbed by the zirconium metal is known from DSC (Sections 2.2.1 and 3.4). What remains of hydrogen must be in the form of a residual zirconium hydride when there is excess hydrogen (Section 4.2.2). Therefore, by varying temperature, the composition of a phase at equilibrium can be determined after an experiment has taken place.

When hydrogen is absorbed from a gas phase at fixed pressure and temperature, the overall driving force can be expressed in terms of thermodynamic parameters [55]. The mass-balance prediction model is then compared to a thermodynamic model to describe the phase boundaries.

4.1. Hydrogen in Copper

Hydrogen in solid solution (SS) in copper forms an equilibrium with hydrogen gas at the metal surface:

Equation 5

An empirical equation known as Sieverts' Law [56], is used to determine the concentration of hydrogen in copper:

$$C_{H \text{ in } Cu} = \left(\frac{2 \cdot M_H}{\rho_{Cu}} \right) \cdot S_{H \text{ in } Cu} \cdot \sqrt{f_{H_2}}$$

Equation 6

where M_H is the molar mass of hydrogen, ρ_{Cu} is the density of copper, $S_{H \text{ in } Cu}$ is the solubility of hydrogen in copper, and f_{H_2} is the fugacity of hydrogen gas. The temperature dependence of solubility is given by:

$$S_{H \text{ in } Cu} = s_{H \text{ in } Cu} \cdot \exp\left(\frac{-\Delta H_S}{R \cdot T}\right)$$

Equation 7

Substituting Equation 7 into Equation 6 and multiplying by the mass of copper gives the mass of hydrogen when the concentration is mass of hydrogen per mass of copper:

$$m_{H \text{ in } Cu} = \left(\frac{2 \cdot M_H}{\rho_{Cu}} \right) \cdot s_{H \text{ in } Cu} \cdot \exp \left(\frac{-\Delta H_S}{R \cdot T} \right) \cdot \sqrt{f_{H_2}} \cdot m_{Cu}$$

Equation 8

Solubility is related to permeation and diffusivity by:

$$S_{H \text{ in } Cu} = \frac{P_{H \text{ in } Cu}}{D_{H \text{ in } Cu}} = \frac{P_o \cdot \exp \left(\frac{-\Delta H_p}{R \cdot T} \right)}{D_o \cdot \exp \left(\frac{-\Delta H_D}{R \cdot T} \right)}$$

Equation 9

The permeation constant is defined as the product of solubility and diffusivity. Permeation is a diffusion experiment where the boundary condition is given by the Sieverts concentration of a pressurised gas. For these experiments, Fick's Law becomes:

$$J = -D_{H \text{ in } Cu} \cdot S_{H \text{ in } Cu} \cdot \nabla p = -P_{H \text{ in } Cu} \cdot \nabla p$$

Equation 10

4.1.1. Hydrogen Fugacity

Hydrogen fugacity, f_{H_2} , is related to hydrogen partial pressure, p_{H_2} , by the empirical relationship³ in units of atmosphere [57]:

$$\ln\left(\frac{f_{H_2}}{p_{H_2}}\right) = C_1 \cdot p_{H_2} - C_2 \cdot p_{H_2}^2 + C_3 \cdot \left(\exp\left(-\frac{p_{H_2}}{300}\right) - 1\right)$$

Equation 11

$$C_1 = \exp\left(-3.8402 \cdot (T)^{\frac{1}{8}} + 0.5410\right)$$

$$C_2 = \exp\left(-0.1263 \cdot (T)^{\frac{1}{2}} - 15.980\right)$$

$$C_3 = 300 \cdot \exp(-0.011901 \cdot T - 5.941)$$

³ Equation C_3 , presented above as a component of Equation 11, has been corrected to agree with tabulated data in the reference [57]. Specifically, -0.011901.

4.2. Mechanical Hydriding Prediction Model

The source of hydrogen in this experiment is epsilon zirconium hydride ($\epsilon\text{-ZrH}_2$), which thermally decomposes to produce hydrogen gas and lower stoichiometric hydrides (ZrH_x). Hydrogen is absorbed by the metals once the internal oxides of the test assemblies have been breached. Hydrogen remains within the test assemblies because of the outer oxide barriers [46]. Hydrogen partitions between zirconium and copper metals, and at equilibrium conservation of mass can be expressed as:

$$\check{m}_{H \text{ in Zr}} + \check{m}_{H \text{ in ZrH}_2} + \check{m}_{H \text{ in Cu}} = \hat{m}_{H \text{ in Zr}} + \hat{m}_{H \text{ in ZrH}_x} + \hat{m}_{H \text{ in Cu}}$$

Equation 12

where $\check{m}_i$ and $\hat{m}_i$ are the total mass of a chemical species before and after mechanical hydriding, respectively. ZrH_x is the residual zirconium hydride powder remaining after the experiment, where $0 \leq x \leq 2$.

At room temperature, using the Sieverts parameters by Magnusson [58], the concentration is 10^{-4} ppm by weight. Thus, the initial amount of hydrogen in copper, $\check{m}_{H \text{ in Cu}}$, is considered negligible.

The final concentration of hydrogen in zirconium is determined after dividing by the mass of zirconium:

$$\hat{C}_{H \text{ in Zr}} = \frac{\check{m}_{H \text{ in Zr}} + (\check{m}_{H \text{ in ZrH}_2} - \hat{m}_{H \text{ in ZrH}_x}) - \hat{m}_{H \text{ in Cu}}}{m_{Zr}}$$

Equation 13

The mass fraction for the initial zirconium hydride powder is given by Equation 2 as $F = \frac{2 \cdot M_H}{M_{ZrH_2}}$, where M_i denotes the molar mass of chemical species i .

The concentration of hydrogen in zirconium after the experiment becomes:

$$\hat{C}_{H \text{ in Zr}} = \frac{\check{m}_{H \text{ in Zr}} + (F \cdot \check{m}_{ZrH_2} - \hat{m}_{H \text{ in ZrH}_x}) - \hat{m}_{H \text{ in Cu}}}{m_{Zr}}$$

Equation 14

Based on the equation above, two distinct cases are possible depending on whether hydrides form in the metal. If hydrides are present then $\hat{m}_{H \text{ in ZrH}_x} > 0$ in Equation 14, otherwise $\hat{m}_{H \text{ in ZrH}_x} = 0$.

4.2.1. No Hydrides in the Metal

Equation 14 is modified for experiments where the concentration of hydrogen in zirconium is insufficient to form hydrides. In this case, there is no residual zirconium hydride powder:

$$\hat{C}_{H \text{ in } Zr} = \frac{\check{m}_{H \text{ in } Zr} + F \cdot \check{m}_{ZrH_2} - \hat{m}_{H \text{ in } Cu}}{m_{Zr}}$$

Equation 15

where $\hat{C}_{H \text{ in } ZrH_x} = \hat{C}_{H \text{ in } Zr}$. The total amount of zirconium metal (m_{Zr}) increases because of the zirconium metal produced from the complete decomposition of the zirconium hydride powder:

$$m_{Zr} = \check{m}_{Zr} + (1 - F) \cdot \check{m}_{ZrH_2}$$

Equation 16

4.2.2. Hydride Formation in the Metal

Hydrogen can be added to the metal above the threshold concentration where hydrides form. The initial zirconium hydride powder decomposes from epsilon phase (ϵ -ZrH₂), becoming a residual hydride with lower stoichiometry (ZrH_x). Gibbs Phase Rule dictates that only one hydride phase can be at equilibrium with hydrogen in solution (α -Zr). This means that the hydride in the metal and the residual hydride interacting with hydrogen in solution must be the same phase. Thus, the hydride in equilibrium with hydrogen in solution cannot be epsilon phase.

The stoichiometry of the residual hydride is unique at a given temperature because there is a single degree-of-freedom:

$$x(T) = \frac{\hat{n}_{H \text{ in } ZrH_x}}{\hat{n}_{Zr \text{ in } ZrH_x}}$$

Equation 17

where n_i represents the number of moles of species i . A plot of $\hat{n}_{H \text{ in } ZrH_x}$ as a function of $\hat{n}_{Zr \text{ in } ZrH_x}$ will have a slope equal to the stoichiometry of the residual hydride at equilibrium at a given temperature as represented in Figure 11. Theoretically, regardless of the amount of ZrH₂ added to a test assembly, $x(T)$ will remain constant.

The horizontal intercept of Figure 11 is a minimum value required for a residual hydride. This value, $h(T) = -b(T)/x(T)$, where $b(T)$ is the vertical intercept, can be converted to a threshold concentration where hydrides first appear in the metal:

$$\hat{C}_{H \text{ in Zr}}^{\text{threshold}} = \frac{\check{m}_{H \text{ in Zr}} + M_{Zr} \cdot h(T) \cdot \left[\frac{F}{1-F} \right] - \hat{m}_{H \text{ in Cu}}}{\bar{m}_{Zr} + M_{Zr} \cdot h(T)}$$

Equation 18

where $\hat{C}_{H \text{ in Zr}}^{\text{threshold}}$ is in grams of hydrogen per gram of zirconium at the equilibrium temperature and $\bar{m}_{Zr}$ is the mean mass of the zirconium discs.

Figure 11 - An example isotherm used to determine the stoichiometry of the residual hydride at a given temperature. A white circle represents a single experiment at the experimental temperature. Black circles are line intercepts. The horizontal intercept is the instance where a residual hydride appears in the metal and as a residual hydride.

Equation 18 gives the minimum concentration to form hydrides in the metal. Concentrations above this limit ($\hat{m}_{H \text{ in } ZrH_x} > 0$) are calculated by substituting,

$$\hat{m}_{H \text{ in } ZrH_x} = \frac{M_{Zr}}{M_H} \cdot x(T) \cdot \check{m}_{Zr \text{ in } ZrH_2} + M_H \cdot b(T)$$

Equation 19

into Equation 14 to give the general prediction model:

$$\hat{C}_{H \text{ in } Zr} = \frac{\check{m}_{H \text{ in } Zr} + F \cdot \check{m}_{ZrH_2} - \left(\frac{M_{Zr}}{M_H} \cdot x(T) \cdot \check{m}_{Zr \text{ in } ZrH_2} + M_H \cdot b(T) \right) - \hat{m}_{H \text{ in } Cu}}{m_{Zr}}$$

Equation 20

when hydrides form in the metal, and residual hydrides are present:

$$x(T) > 0 \text{ and } b(T) > 0;$$

otherwise, Equation 20 reduces to Equation 14 because:

$$x(T) = 0, \quad b(T) = 0, \quad \text{and} \quad m_{Zr} = \check{m}_{Zr} + (1 - F) \cdot \check{m}_{ZrH_2}$$

4.3. Hydrogen Diffusion in Zirconium with Stress

Hydrogen moves interstitially in zirconium with a drift velocity, $\vec{v}$, proportional to a force that can be expressed as a negative gradient in chemical potential:

$$\vec{v} = -\Gamma \cdot \nabla \mu$$

Equation 21

where the proportionality constant, Γ , is the mobility. The flux of hydrogen is the product of the drift velocity and activity (i.e., generalised concentration):

$$\mathbb{J} \equiv \vec{v} \cdot a$$

Equation 22

The chemical potential in a stressed solid is given by:

$$\mu = \mu^0 + RT \cdot \ln(a) + \bar{V} \cdot \sigma$$

Equation 23

where μ^0 is the reference state chemical potential, $\bar{V}$ is the partial molar volume of the solute, and σ is the hydrostatic stress [59]. For constant T , $\bar{V}$, and μ^0 :

$$\nabla \mu = \frac{RT}{a} \cdot \nabla a + \bar{V} \cdot \nabla \sigma$$

Equation 24

Combining these equations yield:

$$\mathbb{J} = -\Gamma \cdot \left(\frac{RT}{a} \cdot \nabla a + \bar{V} \cdot \nabla \sigma \right) \cdot a$$

Equation 25

When there are no stress gradients, Equation 25 reduces to Fick's First Law written in terms of activity:

$$\mathbb{J} = -D \cdot \nabla a$$

Equation 26

Equating Equation 25 with zero stress gradient, and Equation 26, produces the Einstein-Smoluchowski relation:

$$\Gamma = \frac{D}{RT}$$

Equation 27

Substituting Equation 27 into Equation 25 gives:

$$\mathbb{J} = -D \cdot \left(\nabla a + \frac{a \cdot \bar{V} \cdot \nabla \sigma}{RT} \right)$$

Equation 28

Chemical activity is defined by:

$$a = \gamma \cdot C$$

Equation 29

where C is the concentration of the solute and γ is an activity coefficient that accounts for non-ideality.

The activity is approximated by a concentration in the limit of an ideal dilute solute, which will be assumed in accord with the solute in the solid solvent being on the order of 1 atomic-% [20]. Equation 28 becomes:

$$\mathbb{J} = -D \cdot \left(\nabla C + \frac{C \cdot \bar{V}}{RT} \cdot \nabla \sigma \right)$$

Equation 30

This is the Einstein-flux equation. Flux of the solute depends on concentration gradient, and the stress gradient term is known as the drift current. When the chemical potential everywhere is equal, there is no net movement of hydrogen; the flux is zero:

$$\mathbb{J}(T) = 0$$

Equation 31

Three no-flux solutions exist in the presence of hydrides. The trivial solution is when both gradient terms of Equation 30 are zero. The remaining solutions are when both gradient terms are equal and opposite:

$$C_{(-)} = C_{TSS} \cdot \exp \left(-\frac{K \cdot \bar{V} \cdot \sigma}{RT} \right)$$

Equation 32

$$C_{(+)} = C_{TSS} \cdot \exp \left(+\frac{K \cdot \bar{V} \cdot \sigma}{RT} \right)$$

Equation 33

where K is a stress concentration factor, otherwise known as the K-factor [20].

4.4. Gibbs Phase Rule

An infinitesimal change in internal energy of a thermodynamic system can be expressed in terms of temperature, entropy, pressure, volume, and the sum of energy for each component as a function of chemical potential multiplied by its molar mass:

$$dU = T \cdot dS - p \cdot dV + \sum_{i=1}^c \mu_i \cdot dn_i$$

Equation 34

Gibbs free energy is a thermodynamic potential that can be used to calculate the maximum reversible work done on a system:

$$dG = dU + p \cdot dV + V \cdot dp - T \cdot dS - S \cdot dT$$

Equation 35

Substituting Equation 34 into Equation 35 yields:

$$dG = V \cdot dp - S \cdot dT + \sum_{i=1}^c \mu_i \cdot dn_i$$

Equation 36

Gibbs phase rule applies to non-reactive multi-component heterogeneous systems where the thermodynamic criterion of equilibrium is that the chemical potentials of each phase are equal throughout the system [60]. Equilibrium constrains the number of independent intensive variables of the system.

Consider a system of equations based on Equation 36:

$$\begin{bmatrix} dG_1 \\ dG_2 \\ \vdots \\ dG_{C-1} \\ dG_C \end{bmatrix} = V \cdot dp - S \cdot dT + \begin{bmatrix} \mu_1^\alpha & \mu_2^\alpha & \dots & \mu_{C-1}^\alpha & \mu_C^\alpha \\ \mu_1^\beta & \mu_2^\beta & \dots & \mu_{C-1}^\beta & \mu_C^\beta \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \mu_1^{P-1} & \mu_2^{P-1} & \dots & \mu_{C-1}^{P-1} & \mu_C^{P-1} \\ \mu_1^P & \mu_2^P & \dots & \mu_{C-1}^P & \mu_C^P \end{bmatrix} \begin{bmatrix} dn_1 \\ dn_2 \\ \vdots \\ dn_{C-1} \\ dn_C \end{bmatrix}$$

Equation 37

The total number of variables is $P(C - 1) + 2$ because there is P number of phases and only $(C - 1)$ components required to express a system, where the external variables pressure and temperature count as 2 degrees of freedom. If the chemical potential of each component is equal in all phases, the number of constraints reduces to $C(P - 1)$. Gibbs phase rule is a general relation between the degrees-of-freedom, the number of components, and the number of phases at equilibrium:

$$F = P(C - 1) + 2 - C(P - 1) = C - P + 2$$

Equation 38

For systems at constant pressure, Equation 38 reduces to:

$$F = C - P + 1$$

Equation 39

5. Results and Discussion

Sections 5.1 to 5.4 develop a method to add hydrogen quantitatively to zirconium alloys that can be used to approximate reactor end-of-life conditions of hydrogen concentrations and irradiation damage. In these sections, the terms in the mass-balance equation will be presented beginning with the initial hydrogen concentration in zirconium, followed by the stoichiometry of the residual hydride, and the solubility of hydrogen in the copper. These components are combined in the mass-balance equation, and the resulting hydrogen concentration predictions in the zirconium metal are compared with observed measurements.

The results shown in Section 5.5 are used to map the *Zr-H* phase diagram in the range of reactor operating temperatures by contributing data to the delta phase line (δ -ZrH_x) and showing the concentration thresholds for hydride formation in the metal.

Section 5.6 tests the predictions of the *Einstein-McRae-Coleman-Cottrell (EMCC)* model, which is used specifically to reproduce the solvus lines.

In Section 5.7 the implications will be discussed.

5.1. Initial Hydrogen in the Zirconium Metal

The as-received Zircaloy-2 metal sheet was measured by HVE-MS [49] and contains 14 ± 1 ppm of hydrogen (Reference: ACQA# 147829) based on a single collected sample. St. Louis [49] also estimated the initial hydrogen concentration by systematically adding hydrogen to three samples and extrapolating the DSC temperatures in the metal to a value corresponding to no hydrogen addition. The extrapolated DSC temperature was converted to 13.0 ± 2.3 ppm.

The initial concentration of hydrogen in the as-received material can also be determined from the reference samples used in the DSC measurements. Each DSC analysis includes a measurement of the reference sample (see features in Figure 9 indicated by A and H). Four references were randomly selected from the sheet for this study. The hydrogen TSSP MS temperature in these references were measured a total of 90 times and converted into concentration estimates based on McMinn's calibration equation⁴ below 170 °C [17]:

$$C_{H \text{ in Zr}}[\text{ppm}] = 212.1 \cdot \exp\left(-\frac{1003.6}{R \cdot T_{TSSP \text{ MS}}[\text{K}]}\right)$$

Equation 40

⁴ Typically, Equation 4 is used to convert TSSD MS temperature to concentration, however, this equation is less reliable at the lower temperatures ($T < 200$ °C).

The TSSD MS temperature was measured on the first heating run⁵ because of the broader temperature range (depicted by the red dashed line of Figure 10). TSSP was measured on the last cooling run for the same reason.

Table 2 summarises the temperatures and concentrations of the four randomly selected references. The variability is ± 0.8 ppm. Greater standard deviation for the 65.3 mg reference (± 0.5 ppm) is likely because the mass difference between the sample and the reference was typically much larger than for the other references.

Table 2 - Initial hydrogen data for the as-received Zircaloy-2 sheet material

TSSP MS (°C)	TSSD MS (°C)	Observed (ppm)	mass (mg)	measurements
136.0 $\pm$ 5.0	222.8 $\pm$ 4.9	18.3 $\pm$ 0.5	65.3	38
128.2 $\pm$ 2.0	216.3 $\pm$ 1.8	17.4 $\pm$ 0.2	97.3	14
117.2 $\pm$ 0.1	203.5 $\pm$ 2.7	16.2 $\pm$ 0.0	107.3	2
122.5 $\pm$ 1.6	213.8 $\pm$ 1.9	16.8 $\pm$ 0.2	179.1	36
129.0 $\pm$ 3.3	217.8 $\pm$ 3.0	17.5 $\pm$ 0.8	N/A	90

The estimated standard deviation of the initial hydrogen concentration in zirconium measured by DSC is comparable with the uncertainty in the HVE-MS value. Therefore, the initial hydrogen concentration in zirconium is assumed to be 14 ± 1 ppm for the mass-balance prediction models.

⁵ This is contrary to standard procedure where the first run is discarded (Appendix D). These measurements are an exception because the references were all exposed to a constant 10 °C per minute cooling rate prior to heating.

5.2. Hydride Stoichiometry in the Residual Hydride

The stoichiometry of the residual hydride is determined from the slopes in Figure 12, as described in Section 4.2.2. The results are shown in Table 3 for temperatures investigated in this study. A complete overview of the data can be found in Appendix F.

Table 3 - Summary of the observed residual hydride stoichiometry at set temperatures

T (°C)	x(T) = H / Zr	b(T) [mol]	R ²	n
202.9 ± 4.4	1.6747	2.2220E-06	0.9979	8
253.1 ± 4.0	1.6451	-4.5138E-06	0.9813	9
280.3 ± 4.6	1.5122	-7.5495E-06	0.9818	15
299.4 ± 4.6	1.3745	-7.3859E-06	0.9926	3
350.6 ± 5.3	1.4889	-3.0870E-05	0.9898	14

Figure 12 - Isotherms of residual zirconium hydride

5.3. Quantifying the Solubility of Hydrogen in Copper

Few direct measurements exist for hydrogen solubility in copper below 500 °C [58], necessitating extrapolations from higher temperatures. Figure 13 and Figure 14 illustrate the diversity of predictions made of hydrogen solubility in copper.

Figure 13 - Predicted solubilities of hydrogen in copper determined from extrapolations of high-temperature measurements. Also shown is the solubility determined by the permeability divided by diffusivity [58], and the results of this study.

Solubility parameters in this study were determined by a regression of observed hydrogen concentrations in the zirconium metal to the general prediction model (Equation 20) with the Sieverts' relation (Equation 8). The solubility of hydrogen in copper between 200 °C and 450 °C was found to be:

$$S_{H \text{ in } Cu} = (720 \pm 80) \left[\frac{\text{mol H}_2}{\text{m}^3 \text{ Cu}} \cdot \text{MPa}^{-\frac{1}{2}} \right] \cdot \exp \left(\frac{-(42.0 \pm 0.6) [\text{kJ/mol}]}{R \cdot T[\text{K}]} \right)$$

Equation 41

The Sieverts' constants of Equation 41 are consistent with the relation $S = P / D$ (Equation 9), given the permeation and diffusion equations from Magnusson [58]. The theoretical solubility can be expressed as:

$$S_{H \text{ in } Cu} = 810 \left[\frac{\text{mol H}_2}{\text{m}^3 \text{ Cu}} \cdot \text{MPa}^{-\frac{1}{2}} \right] \cdot \exp \left(\frac{-42.3 [\text{kJ/mol}]}{R \cdot T[\text{K}]} \right)$$

Equation 42

The diffusivity equation reported by Magnusson [58] includes measurements over 6 orders of magnitude, and permeability equation is derived from data spanning 10 orders of magnitude. Both equations cover the temperature range of 25 °C to 730 °C so that extrapolation is not required. The Sieverts' relationship determined in this study⁶ is within one standard error of the theoretical value (Figure 14) given by $S = P / D$.

⁶ Notice the consistency and proximity of this study to the theoretical value as compared to other results shown in Figure 14. This study determines the solubility without extrapolation.

Figure 14 - The deviation of hydrogen solubility in copper predictions and the observations made from $S = P / D$ database [58]. The yellow band is one standard error for the Sieverts' relation determined in this study, which is consistent with the ratio of permeability and diffusivity, as indicated by 0 %.

5.4. Mass-Balance Compared with Observations

The concentrations of hydrogen in the Zircaloy-2 discs were converted from the observed DSC MS temperatures by Equation 4. These concentrations were compared with the predictions of Equation 20 combined with the results of Sections 5.1 to 5.3: the initial hydrogen in the as-received zirconium metal, 14 ± 1 ppm; the stoichiometry of the residual hydride, Table 3; and the solubility of hydrogen in copper, Equation 41.

Figure 15 shows that the mass-balance fully accounts for hydrogen in the experiment: the slope of the line is 0.99 ± 0.03 with an $R^2 = 0.94$ for 72 data points⁷.

⁷ In other words, the predictions are 99 % accurate with a precision of 3 %.

Figure 15 - Mass-balance predictions (Equation 20) compared with concentrations of hydrogen in Zircaloy-2 samples calculated from DSC temperatures. Black diamonds are experiments that contain no hydrides in the metal, which are mainly attributed to St. Louis [49]. White circles represent experiments where hydrides have formed in the metal, and a residual hydride powder remains.

5.5. Zirconium-Hydrogen Phase System

5.5.1. Gamma (γ -ZrH) and Delta (δ -ZrH_x) Phase Region

The five stoichiometries from Table 3, based on 53 measurements, are plotted as the delta phase boundary in the phase diagram shown in Figure 16. Literature results have been plotted for comparison.

The gamma (γ -ZrH) solvus represented in *Figure 16* exists at temperatures as high as 350.6 ± 5.3 °C and is expected to continue to higher temperatures. This expectation is reinforced by research from Gulbransen [24], who used a combination of XRD and a microbalance to measure a specimen having a stoichiometry associated with the gamma phase boundary.

Figure 16 - Updated delta phase solvus (δ -ZrH_x) indicated by the golden triangles for the Zr-H system. The K-factor for the EMCC C+ model was calculated to be 1.80 ± 0.06 . Vertical dotted lines define where stable hydride configurations exist [30].

5.5.1.1. Gamma-to-Delta Phase Transition

DSC measurements of the TSSD MS were converted into expected concentration with Equation 4. Linear regression was applied to relate these estimates to the TSSP OS temperature measurements. Figure 17 marks outliers with a black cross when data points are more than two standard deviations from the regression line.

Figure 17 - TSSP OS temperature measured by DSC compared with HVE-MS concentration

TSSP OS temperature deviates from this linear trend (Figure 17) at both temperature extremes⁸. For lower temperatures, the deviation appears between 165 °C ($2.28 = 1000/T[K]$) and 197 °C ($2.13 = 1000/T[K]$). This observation is congruent with Root's [42] measurement (187 ± 10 °C from Figure 6) made by neutron diffraction. A similar deviation was reported by McMinn [17] at 170 °C using DSC⁹.

From Figure 16, it seems that the stoichiometry in the temperature range of the deviation is approximately 1.75, which is the stoichiometry of the most stable delta hydride ($\delta\text{-Zr}_4\text{H}_7$) structure theoretically determined [30]. Thus, below the deviation temperature gamma ($\gamma\text{-ZrH}$) and epsilon ($\epsilon\text{-ZrH}_2$) hydrides are expected, and above, gamma and delta ($\delta\text{-ZrH}_x$) hydrides.

⁸ For higher temperatures, McMinn's calibration equation (Equation 4) [17] was derived from data in the temperature range 170 °C to 325 °C. Hence, deviation at higher temperatures is not unexpected (Figure 17).

⁹ McMinn [17] proposed that DSC analysis requires two regression fits to describe TSSP MS temperature to concentration. Hence, Equation 40 converts TSSP MS temperatures that are below 170 °C.

5.5.2. Regions where Hydrides form in the Metal

From Figure 12, the stoichiometry (Table 3) of the residual hydride was determined from the slopes for each isotherm studied. From the horizontal intercepts, the minimum amount of zirconium hydride powder required to observe hydrides in the metal can be calculated with Equation 18 (Section 4.2.2). Above this threshold, a residual hydride remains. These results are presented in Table 4, and Figure 18, indicated by yellow circles and error bars.

Table 4 - The threshold concentration that defines hydrogen in solution and hydrides

n	T(°C)	threshold (ppm)
8	202.9 ± 4.4	18.3
9	253.1 ± 4.0	45.4
15	280.3 ± 4.6	55.4
3	299.4 ± 4.6	73.0
14	350.6 ± 5.3	123.1

Figure 18 - TSSP OS measurements as a function of concentration evaluated by HVE-MS. Yellow circles are the threshold concentrations in Table 3. Other observations are conditions for DHC initiation on cooling [20].

5.6. EMCC Model Comparison

There are three no-flux solutions to Equation 30 when hydrides are present (Section 4.3):

- The no-gradient solution represents TSSP OS in Figure 18;
- $C_{(-)}$ (Equation 32) is the concentration of hydrogen where hydrides first appear, which is shown as the yellow circles and yellow dashed line in Figure 18;
- $C_{(+)}$ (Equation 33, Figure 16) is the concentration of hydrogen that stabilize gamma hydrides (γ -ZrH). When the concentration of hydrogen reaches values sufficient to satisfy delta phase stoichiometry (i.e., the x in δ -ZrH $_x$), then hydrogen can precipitate. The delta phase is given by $[C_{(+)} / C_{TSS}]$, shown as the gold dashed line Figure 16.

Equation 32 and Equation 33 depend on a stress concentration factor (K) known as the K-factor, yield strength ($\sigma(T)$), and partial molar volume ($\bar{V}$) of hydrogen in zirconium.

For this thesis, the yield strength (MPa) as a function of temperature for Zircaloy-2 is given by [20]:

$$\sigma(T) = 959 - 1.95 \cdot T(^{\circ}\text{C})^2 + (2.77 \cdot 10^{-3}) \cdot T(^{\circ}\text{C})$$

Equation 43

The partial molar volume is taken as $1.7 \times 10^{-6} \text{ m}^3 / \text{mol H}$ [61] [45] [62]. It is assumed constant over the experimental conditions.

The K-factor (K) was determined by least-squares regression of the $C_{(+)}$ model (Equation 33), taking into account the stoichiometries in Table 3, with exception of the 300.4 °C observation, as discussed in Section 5.5.1. The K-factor was determined to be 1.80 ± 0.06 , which is within the expected range of 1 to 2.4 calculated by Hutchinson [63] [64].

The resulting $C_{(+)}$ stoichiometry model is plotted as the gold dashed line in Figure 16 over the temperature range of the experiments. The line extrapolates to the stoichiometric ratio of 1.75 at 184.8 ± 2.3 °C. This ratio corresponds with the stable delta hydride $\delta\text{-Zr}_4\text{H}_7$ [30] as discussed in Section 5.5.1. At this temperature, a horizontal line is expected to connect the gamma ($\gamma\text{-ZrH}$) and epsilon ($\epsilon\text{-ZrH}_2$) phases.

The same determined value of K , was used to plot the yellow dashed $C_{(-)}$ curve in Figure 18. The same formalism can account for the delta phase solvus ($\delta\text{-ZrH}_x$) and the threshold concentrations.

5.7. Implications

The general mass-balance model predicts hydrogen concentrations in Zircaloy-2 with an accuracy of 99 % and 3 % precision.

Confidence in the model is reinforced by the determined Sieverts' parameters of hydrogen in copper. Extrapolations made from direct measurements at high-temperatures reported in other studies disagree with one another and do not satisfy the theoretical relation that solubility is equal to permeability divided by diffusivity (Section 5.3). The solubility equation determined in this study is within one standard error of the theoretical expectation that was interpolated from data spanning up to 10 orders of magnitude (Figure 14). Recall that the hydrogen content in each component, including copper, depends on the other components in the system. The Sieverts' relationship is highly sensitive to errors from other components (Zr , ZrH_2 , ZrH_x) in the mass-balance equation because the amount of hydrogen going into the copper accounts for less than 5 % of the total mass of the test assembly.

The determined stoichiometric ratios agree with other reported values (Figure 16). Regardless of the amount of zirconium hydride added, the stoichiometry of the residual hydride is a constant value at a specific temperature (Figure 12), in accord with Gibbs Phase Rule with one degree-of-freedom.

The threshold concentrations (Equation 18, Table 4), based on the mass-balance equation, agree with DHC initiation concentrations on cooling (Figure 18). The experiments to determine the thresholds were heated to the test temperature. There will be regions in the bulk of the metal under tensile stress, such as at dislocations and grain boundaries, that act similarly to cracks tips under load. Hydrides form in these regions as they do at crack tips. Regardless of heating or cooling, the threshold concentration and temperature for hydride formation is the same, suggesting that there is no hysteresis, contrary to the standard interpretation presented in Section 2.2.1.

The gamma-to-delta phase transition reported by Root [42] at 180 °C, and in this study at 184.8 ± 2.3 °C (Figure 16), is mirrored in Figure 18. DHC initiation concentrations from Coleman [65] are shifted to the left of the $C_{(-)}$ curve extrapolated to temperatures below 200 °C. In addition, there is an indication that the DSC TSSP OS is discontinuous at a similar temperature (Figure 17). This observation is consistent with the discontinuity reported by McMinn where two equations are needed to relate DSC TSSP MS temperatures to HVE-MS concentrations below (Equation 40) and above (Equation 4) 170 °C [17].

Adding hydrogen to removed CANDU pressure tubing to end-of-life concentrations without annealing irradiation damage should be done below 300 °C [18] as described in Section 2.1.3. Concentrations beyond 50 ppm have been added at 202.9 ± 4.4 °C for 22 hours with mechanical hydriding. The technique is expected to work as low as 184.8 ± 2.3 °C and for shorter times. Furthermore, the hydrogen addition process can be repeated multiple times by replenishing the zirconium hydride powder so that higher concentrations can be achieved.

From the experimental results of this thesis alone, there is insufficient information to support including a vertical gamma phase (γ -ZrH) line at $x = 1$ on the binary phase. The mass-balance equation does not distinguish between the hydride phase at equilibrium with hydrogen in solution.

Support for including the gamma phase line comes from the consistency of the EMCC predictions with the experimental delta phase stoichiometries and threshold concentrations determined in this study, which are consistent with the XRD result reported by Gulbransen [24], the DHC initiation results shown in Figure 18, and hydrides that dissolve on cooling and form on heating observed by XRD [20]. The success of the EMCC model suggests the potential to describe other phase boundaries.

6. Concluding Remarks

The objectives from Section 1.1 are listed below with concluding remarks:

- i. *Develop a method to add hydrogen quantitatively to zirconium alloys that can be used to approximate reactor end-of-life conditions of hydrogen concentrations and irradiation damage:*

The mechanical hydrogen addition method can be used to add hydrogen with 3 % precision based on mass-balance, which accounts for the hydrogen in the copper, zirconium, and the residual hydride powder when it exists. Mechanical hydriding can add hydrogen to zirconium alloys at 200 °C in 22 hours, which allows hydrogen addition to reactor end-of-life concentrations without annealing irradiation damage.

ii. Map the Zr-H phase diagram in the range of reactor operating temperatures, specifically:

- o α -Zr, the Terminal Solid Solubility (TSS)
- o γ -ZrH (Is it metastable?)
- o δ -ZrH_x
- o ϵ -ZrH₂

Measurements from this study have contributed to the thermodynamic description of the Zr-H phase diagram in the temperature range of a nuclear reactor. The delta (δ -ZrH_x) solvus has been measured and compares well with literature values. The TSS is defined by TSSP OS where there is no gradient of stress nor of concentration at the hydride-metal interface at equilibrium. An additional equilibrium line corresponds to threshold concentrations where hydrides form at local tensile stress risers in the metal. The gamma phase boundary (γ -ZrH) has to be determined. A gamma-to-delta phase transition has been confirmed to exist at 184.8 ± 2.3 °C.

iii. *Test predictions of the Einstein-McRae-Coleman-Cottrell (EMCC) model:*

The observed measurements of delta phase (δ -ZrH_x) stoichiometry and threshold concentrations (Figure 16 and Figure 18) can be described with the EMCC model using a K of 1.80 ± 0.06 . The model has the potential to define other phase boundaries.

In addition to the objectives of this thesis, the hydrogen solubility in copper has been determined between 200 °C to 450 °C (Equation 41). It was found to agree with the theoretical solubility (Equation 15).

6.1. Recommendations and Future Work

Recall that data plotted in Figure 17 diverges at both temperature extremes from the linear regression fit. Given the significance of the gamma-to-delta phase transformation identified as 185 °C at lower temperatures, it would be worth investigating stoichiometry above 350 °C to determine if another change in material properties occurs.

The yield strength of Zircaloy-2 as a function of temperature above 350 °C also needs to be examined to extend the EMCC model to higher temperatures. It could be that the divergence observed in Figure 17 is related to the change in yield strength of the metal at elevated temperatures [17].

Figure 16 suggests that the region between the gamma and epsilon phase boundaries could have additional phase boundaries associated with various stable delta phases. The stoichiometry of the residual hydride slightly deviates at 250 °C and 300 °C relative to other neighbouring data shown in Figure 16. There is a possibility that these points are not affiliated with a single delta phase boundary based on similar stoichiometry reported by Moore [35]. Additional stoichiometry data in this region should be collected.

References

- [1] Y. Zhong and D. D. MacDonald, "Thermodynamics of the Zr-H binary system related to nuclear fuel sheathing and pressure tube hydriding," vol. 423, no. 1-3, 2012.
- [2] CNSC, "Fitness for service," 15 03 2018. [Online]. Available: <http://nuclearsafety.gc.ca/eng/resources/research/fitness-for-service.cfm>. [Accessed 11 April 2018].
- [3] IESO, "Supply Overview," 2018. [Online]. Available: <http://www.ieso.ca/en/power-data/supply-overview/transmission-connected-generation>. [Accessed 05 April 2018].
- [4] Canadian Standards Association, "Technical Requirements for In-service Evaluation of Zirconium Alloy Pressure Tubes in CANDU Reactors," 2005.
- [5] Ontario Energy Board, "Electricity rates," 2018. [Online]. Available: <https://www.oeb.ca/rates-and-your-bill/electricity-rates>. [Accessed 05 April 2018].
- [6] Nuclear Energy Agency, "Nuclear Fuel Behaviour in Loss-of-coolant Accident (LOCA) Conditions," OECD, Paris, France, 2018.
- [7] D. A. Meneley and Y. Q. Ruan, "Introduction to CANDU 6," in *Xi'an Jiaotong University*, 1998.
- [8] J. C. Simpson and C. E. Ells, "Delayed Hydride Embrittlement in Zr-2.5 wt-% Nb," vol. 52, 1974.
- [9] E. C. W. Perryman, "Pickering Pressure Tube Cracking Experience," vol. 17, no. 2, pp. 95-105, 1978.
- [10] D. Schrire, B. Grapengiesser, L. Hallstadius, I. Lundholm, G. Lysell, G. Frenning, G. Ronnberg and A. Jonsson, "Secondary Defect Behavior in ABB BWR Fuel," in *International Topical Meeting on LWR Fuel Performance*, West Palm Beach, 1994.
- [11] K. Edsinger, J. H. Davies and R. B. Adamson, "Degraded Fuel Cladding Fractography of Fracture Behavior," in *Zirconium in the Nuclear Industry - Twelfth International Symposium*, West Conshohocken, PA, 2000.
- [12] K. Sakamoto, M. Nakatsuka and T. Higushi, "Simulation of Cracking during Outside-in Type Failure of High Burn-up Fuel Cladding Tubes," in *Water Reactor Fuel Performance Meeting*, Seoul, Korea, 2008.
- [13] C. E. Coleman, G. A. McRae and B. W. Leitch, "Evaluating the risk of delayed hydride cracking in components made

- from zirconium alloys," Eighth ATI Corrosion Solutions Conference, Lake Louis, Alberta, Canada, 2011.
- [14] CNSC, "Future Directions for Using the Leak-Before-Break Concept in Regulatory Assessments," CNSC, 2009.
 - [15] G. D. Moan, C. E. Coleman, E. G. Price, D. K. Rodgers and S. Sagat, "Leak-Before-Break in the Pressure Tubes of CANDU Reactors," vol. 43, 1990.
 - [16] B. A. Cheadle, A. Celovsky, M. Ghafoor and W. Butt, "Assessment of the Integrity of KANUPP Fuel Channels," in *CNA/CNS Conference*, Fredricton, New Brunswick, 1996.
 - [17] A. McMinin, E. C. Darby and J. S. Schofield, "The Terminal Solid Solubility of Hydrogen in Zirconium Alloys," in *Zirconium in the Nuclear Industry: Twelfth International Symposium*, West Conshohocken, Pennsylvania, USA, 2000.
 - [18] C. E. Coleman, C. K. P. Chow, C. E. Ells, M. Griffiths, E. F. Ibrahim and S. Sagat, "Rejuvenation of Fracture Properties of Irradiated Zr-2.5Nb by Heat Treatment," in *Effects of Radiation on Materials*, vol. 15th International Symposium, ASTM, 1992.
 - [19] V. A. Sieverts and E. Roell, "Zirkonium, Thorium und Wasserstoff," *Zeitschrift für anorganische und allgemeine Chemie*, vol. 153, no. 1, pp. 289-308, 1926.
 - [20] G. A. McRae and C. E. Coleman, "Precipitates in metals that dissolve on cooling and form on heating: An example with hydrogen in alpha-zirconium," vol. 499, pp. 622-640, February 2018.
 - [21] E. Königsberger, G. Eriksson and W. A. Oates, "Optimisation of the thermodynamic properties of the Ti-H and Zr-H systems," vol. 299, no. 1-2, 2000.
 - [22] W. H. Erickson and D. Hardie, "The Influence of Alloying Elements on the Terminal Solid Solubility of Hydrogen in alpha-Zirconium," vol. 13, no. 2, pp. 254-262, 1964.
 - [23] E. A. Gulbransen and K. F. Andrew, "Crystal Structure and Thermodynamic Studies on the Zirconium-Hydrogen Alloys," vol. 101, no. 9, pp. 474-480, 1954.
 - [24] E. A. Gulbransen and K. F. Andrew, "Solubility and decomposition pressures of hydrogen in alpha-zirconium," *The Journal of Minerals, Metals and Materials Society*, vol. 7, no. 1, pp. 136-144, January 1955.
 - [25] C. E. Ells and A. D. McQuillan, "A study of the hydrogen-pressure relationships in the zirconium-hydrogen system," vol. 85, no. 3, pp. 89-96, 1956-1957.
 - [26] J. W. Gibbs, "On Equilibrium of Heterogeneous Substances," vol. 3, no. 1-2, 1874-1878.

- [27] G. C. Weatherly, "The Precipitation of gamma-Hydride Plates in Zirconium," vol. 29, no. 3, pp. 501-512, 1980.
- [28] K. E. Moore, "Phase Relationships in the Alpha + Delta Region of the Zr-H System," vol. 27, no. 3, pp. 46-56, 1969.
- [29] T. B. Douglas, "High-Temperature Thermodynamic Functions for Zirconium and Unsaturated Zirconium Hydrides," vol. 67A, no. 5, 1963.
- [30] M. Christensen, W. Wolf, C. Freeman, E. Wimmer, R. B. Adamson, L. Hallstadius, P. E. Cantonwine and E. V. Mader, "H in alpha-Zr and in zirconium hydrides: solubility, effect on dimensional changes, and the role of defects," vol. 27, no. 2, 2015.
- [31] S. Mishra, K. S. Sivaramakrishnan and M. K. Asundi, "FORMATION OF THE GAMMA PHASE BY A PERITECTOID REACTION IN THE ZIRCONIUM-HYDROGEN SYSTEM," *Journal of Nuclear Materials*, vol. 45, no. 3, pp. 235-244, 1972-1973.
- [32] B. A. Kalin, P. A. Platonov and Y. V. Tuzov, "Structural Materials for nuclear engineering," vol. 6, 2012.
- [33] L. D. La Grange, L. J. Dykstra, J. M. Dixon and U. Merten, "A Study of the Zirconium-Hydrogen and Zirconium-Hydrogen-Uranium Systems between 600 and 800 degrees," vol. 63, no. 12, 1959.
- [34] J. J. Kearns, "Terminal Solubility and Partitioning of Hydrogen in the Alpha Phase of Zirconium, Zircaloy-2 and Zircaloy-4," vol. 22, no. 3, 1967.
- [35] K. E. Moore and W. A. Young, "Phase studies of the Zr-H system at high hydrogen concentrations," vol. 27, no. 3, pp. 316-324, 1968.
- [36] R. L. Beck, "Zirconium-Hydrogen Phase System," vol. 55, 1962.
- [37] G. G. Libowitz, "A Pressure-Composition-Temperature Study of the Zirconium-Hydrogen System at High Hydrogen Contents," vol. 5, no. 2, pp. 228-233, 1961.
- [38] L. Espagno, P. Azou and P. Bastien, "Dilatometric study of the zirconium-hydrogen system between ambient and 500 C," vol. 248, pp. 2003-2005, 1959.
- [39] L. Espagno, P. Azou and P. Bastien, "Dilatometric study of the zirconium-hydrogen system," vol. 247, pp. 1199-1202, 1958.
- [40] D. A. Vaghan and J. R. Bridge, "High-temperature X-ray diffraction investigation of the Zr-H system," vol. 8, pp. 528-531, 1956.

- [41] M. N. A. Hall, S. L. H. Martin and A. L. G. Rees, "The solubility of hydrogen in zirconium and zirconium-oxygen solid solutions," vol. 41, pp. 306-316, 1945.
- [42] J. H. Root and R. W. L. Fong, "Neutron diffraction study of the precipitation and dissolution of hydrides in Zr-2.5Nb pressure tube material," vol. 232, no. 1, pp. 75-85, 1996.
- [43] T. Maimaitiyili, C. Bjerken, A. Steuwer, Z. Wang, J. Daniels, J. Andrieux, J. Blomqvist and O. Zanellato, "In situ observation of the gamma-ZrH formation by X-ray diffraction," vol. 695, pp. 3124-3130, 2017.
- [44] Z. Wang, A. Steuwer, N. Liu, T. Maimaitiyili, M. Avdeev, J. Blomqvist, C. Bjerken, C. Curfs, J. A. Kimpton and J. E. Daniels, "Observations of temperature stability of gamma-zirconium hydride by high-resolution neutron powder diffraction," vol. 661, pp. 55-61, 2016.
- [45] A. I. Kolesnikov, A. M. Balagurov, I. O. Bashkin, V. K. Fedotov, V. Y. Malyshev, G. M. Mironova and E. G. Ponyatovsky, "A real-time neutron diffraction study of phase transitions in the Ti-D system after high-pressure treatment," *Journal of Physics: Condensed Matter*, vol. 5, no. 29, pp. 5045-5058, 1993.
- [46] D. T. Peterson and H. M. Herro, "Partial Molar Volumes of Hydrogen and Deuterium in Niobium, Vanadium, and Tantalum," *Metallurgical Transactions A*, vol. 14A, no. 1, 1983.
- [47] ASTM, "Standard Specification for Hot-Rolled and Cold-Finished Zirconium and Zirconium Alloy Bars, Rod, and Wire for Nuclear Application," ASTM International, 2013.
- [48] Sigma-Aldrich, "Product Specification: Zirconium(II) hydride -- 325 mech, 99 %," Saint Louis, Missouri, USA, 2014.
- [49] C. St. Louis, "A Novel Technique for the Addition of Hydrogen to Zirconium Alloys: Mechanical Hydrogen Ingress and its Applications," Ottawa-Carleton Institute for Mechanical and Aerospace Engineering, Ottawa, 2015.
- [50] Mettler Toledo, "Know your safe weighing range with good weighing practice," Mettler Toledo, Greifensee, Switzerland, 2017.
- [51] K. Tashiro, June 2006. [Online]. Available: https://cns-snc.ca/media/pdf_doc/awards/2006_awards/InnovativeAchievementAward-K_Tashiro.pdf.
- [52] NETZSCH Group, "Differential Scanning Calorimetry - DSC 404 F1/F3 Pegasus®," NETZSCH, Selb, 2016.

- [53] CNL, "DSC Calibration Record Master 2007," Chalk River, 2007.
- [54] M. Luisi, "Characterizing the measurement uncertainty of a high-temperature heat flux differential scanning calorimeter," Graz University of Technology, 2014.
- [55] R. A. Oriani and M. Lahaina, "The Physical and Metallurgical Aspects of Hydrogen in Metals," in *Fourth International Conference on Cold Fusion*, Palo Alta, California, USA, 1993.
- [56] A. Sieverts, „Absorption of Gases by the Metals," Bd. 21, pp. 37-46, 1929.
- [57] H. R. Shaw and D. R. Wones, "Fugacity Coefficients for Hydrogen Gas between 0 ° and 1000 °C, for Pressures to 3000 atm," vol. 262, no. 7, pp. 918-929, 1964.
- [58] H. Magnusson and K. Frisk, "Diffusion, Permeation and Solubility of Hydrogen in Copper," vol. 38, no. 1, 2017.
- [59] J. C. M. Li, R. A. Oriani and L. S. Darken, "The Thermodynamics of Stress Solids," *Zeitschrift für Physikalische Chemie*, vol. 49, pp. 271-290, 1966.
- [60] P. Atkins and J. de Paula, *Physical Chemistry: Eighth Edition*, Freeman & Company, W. H., 2006, p. 1072.
- [61] S. R. MacEwen, C. E. Coleman and C. E. Ells, "Dilation of HCP zirconium by interstitial deuterium.pdf," *Acta Metallurgica*, vol. 33, no. 5, pp. 753-757, 1985.
- [62] A. A. Shmakov, B. A. Kalin and A. G. Ioltukhovskii, "A theoretical study of the kinetics of hydride cracking in zirconium alloys," vol. 45, no. 7-8, pp. 315-320, 2003.
- [63] J. W. Hutchinson, "Singular Behaviour at the End of a Tensile Crack in a Hardening Material," *Journal of the Mechanics and Physics of Solids*, vol. 16, pp. 13-31, 1967.
- [64] J. R. Rice and G. F. Rosengren, "Plane Strain Deformation near a Crack Tip in a Power-law Hardening Material," vol. 16, pp. 1-12, 1968.
- [65] C. E. Coleman and J. F. R. Ambler, vol. 17, no. 4, pp. 81-84, 1978.
- [66] S. Sōmiya, *Hydrothermal Reactions for Materials Science and Engineering: An Overview of Research in Japan*, Japan: Elsevier Science, 1989.
- [67] C. Hyun-Jin, J. Ki-Nam, A. Ji-Hyeong and K. Kyu-Tae, "The effect of hydrogen and oxygen contents on hydride reorientations of zirconium alloy cladding tubes," vol. 47, no. 6, pp. 746-755, 2015.
- [68] E. O. Braaten and G. F. Clark, "The diffusion of hydrogen through copper," 1935.

- [69] W. R. Ham, "The diffusion of hydrogen through oxygen-free copper," *Journal of Chemical Physics*, vol. 7, pp. 903-907, October 1939.
- [70] J. Belle and M. W. Mallett, "Kinetics of high temperature oxidation of zirconium," *Journal of the Electrochemical Society*, pp. 339-342, July 1954.
- [71] W. Eichenauer and A. Pebler, "Measurement of the diffusion coefficient and the solubility of hydrogen in aluminum and copper," *Zeitschrift für Metallkunde*, vol. 48, no. 7, pp. 373-378, 1957.
- [72] C. E. Holley, W. J. Worlton and R. K. Zeigler, "Compressibility factors and fugacity coefficients calculated from the Beattie-Bridgeman equation of state for hydrogen, nitrogen, oxygen, carbon dioxide, ammonia, methane, and helium," U. S. Atomic Energy Commission, New Mexico, 1959.
- [73] G. Ostberg, "Determination of hydride solubility in alpha phase zirconium, zircaloy-2 and zircaloy-4," *Journal of Nuclear Materials*, vol. 5, no. 2, pp. 208-215, August 1962.
- [74] G. Ostberg, "Metallographic study of the isothermal transformation of beta phase in zircaloy-2," Aktiebolaget Atomenergi, Stockholm, 1960.
- [75] B. Siegel, "Hydride formation by atomic hydrogen reactions," *Journal of Chemical Education*, vol. 38, no. 10, pp. 496-501, 1961.
- [76] MTS Systems Corporation, "MTS 810 & 858 Material Testing Systems," Eden Prairie, 2006.
- [77] D. R. Wones and H. R. Shaw, "Fugacity coefficients for hydrogen gas between 0 ° and 1000 °C, for pressures to 3000 atm*," *American Journal of Science*, no. 262, pp. 918-929, 1964.
- [78] X. Hu, K. A. Terrani and B. D. Wirth, "Hydrogen desorption kinetics from zirconium hydride and zirconium metal in vacuum," *Journal of Nuclear Materials*, vol. 448, no. 1-3, pp. 87-95, January 2014.
- [79] J. Crank, *Mathematics of Diffusion*, Second ed., Bristol, England: Oxford University Press, 1975.
- [80] R. N. Singh, R. Kameswaran and B. Gopalan, "Hydrogen Charging, Hydrogen Content Analysis and Metallographic Examination of Hydride in Zirconium Alloys," Government of India, Mumbai, 2003.
- [81] R. L. Eadie, K. Tashiro, D. Harrington and M. Leger, "The Determination of Partial Molar Volume of Hydrogen in

- Zirconium in a Simple Stress Gradient using Comparative Microcalorimetry," *Scripta Metallurgica et Materialia*, vol. 26, pp. 251-256, 1992.
- [82] C. E. Coleman and J. F. R. Ambler, "Solubility of Hydrogen Isotopes in Stressed Hydride-Forming Metals," *Scripta Metallurgica*, vol. 17, pp. 77-82, 1983.
 - [83] J. S. Tolliver and M. Reeves, "Diffusion in a Hollow Cylinder," Union Carbide Corporation, Oak Ridge, 1978.
 - [84] J. B. Brady, "Diffusion Data for Silicate Minerals, Glasses, and Liquids," American Geophysical Union, Northampton, 1995.
 - [85] R. M. Barrer, *Diffusion in and Through Solids*, 2 ed., vol. 1, London: Cambridge University Press, 1951.
 - [86] H. S. Carslaw, *The Mathematical Theory of the Conduction of Heat in Solids*, Second ed., vol. 1, London: MacMillan and Co., Limited, 1921.
 - [87] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Second ed., vol. 1, London: Oxford University Press, 1959.
 - [88] G. A. McRae and C. E. Coleman, "The First Step in Delayed Hydride Cracking in Zirconium Alloys," *Journal of Nuclear Materials*, vol. 396, no. 1, pp. 130-143, January 2010.
 - [89] D. Rodgers, M. Griffiths, G. Bickel, A. Buyers, C. Coleman, H. Nordin and S. St. Lawrence, "Performance of Pressure Tubes in CANDU Reactors," *CNL Nuclear Review*, 2015.
 - [90] S. Sagat, C. E. Coleman, M. Griffiths and B. J. S. Wilkens, "The Effect of Fluence and Irradiation Temperature on Delayed-Hydride-Cracking in Zr-2.5Nb," in *Zirconium in the Nuclear Industry: Tenth International Symposium*, 1994.
 - [91] D. K. Rodgers, C. E. Coleman, M. Griffiths, G. A. Bickel, J. R. Theaker, I. Muir and A. A. Bahurmuz, "In-reactor performance of pressure tubes in CANDU reactors," vol. 383, 2008.
 - [92] J. H. Root, W. M. Small, D. Khatamian and O. T. Woo, "Kinetics of the delta to gamma zirconium hydride transformation in Zr-2.5Nb," vol. 51, no. 7, 2003.
 - [93] "Operating Instructions: ALC Models," Acculab Sartorius Group.
 - [94] R. L. Eadie and E. C. C., "Effect of stress on hydride precipitation in zirconium-2.5% niobium and on delayed hydride cracking," vol. 23, no. 11, pp. 1865-1870, 1989.

- [95] C. E. Coleman and J. F. R. Ambler, "Solubility of Hydrogen Isotopes in Stressed Hydride-Forming Metals," vol. 17, pp. 77-82, 1983.
- [96] W. M. Small, J. H. Root and D. Khatamian, "Observation of kinetics of gamma zirconium hydride formation in Zr-2.5Nb by neutron diffraction," *Journal of Nuclear Materials*, vol. 256, no. 2-3, pp. 102-107, 1998.
- [97] E. Zuzek, "On Equilibrium in the Zr-H System," vol. 28, no. 3-4, pp. 323-338, 1986.
- [98] W. E. Wang and D. R. Olander, "Thermodynamics of the Zr-H System," *Journal of the American Ceramic Society*, vol. 78, no. 12, pp. 3323-3328, 1995.
- [99] N. Dupin, I. Ansara, C. Servant, C. Toffolon, C. Lemaignan and J. C. Brachet, "Thermodynamic database for zirconium alloys," vol. 275, no. 3, pp. 287-295, 1999.
- [100] L. Lanzani and M. Ruch, "Comments on the stability of zirconium hydride phases in Zircaloy," *Journal of Nuclear Materials*, vol. 324, no. 2-3, pp. 165-176, 2004.
- [101] H. Horinouchi, M. Shinohara, T. Otsuka, K. Hashizume and T. Tanabe, "Determination of hydrogen diffusion and permeation coefficients in pure copper at near room temperature by means of tritium tracer techniques," vol. 580, no. 1, 2013.
- [102] S. C. Marchi and B. P. Somerday, "Technical Reference of Hydrogen Compatibility of Materials: Copper Alloys," Sandia National Laboratories, Livermore, California, USA, 2006.
- [103] C. L. Whitmarsh, "Review of Zircaloy-2 and Zircaloy-4 Properties Relevant to N. S. Savannah Reactor Design," Oak Ridge National Laboratories, Oak Ridge, Tennessee, USA, 1962.
- [104] R. N. Singh, R. Kishore, T. K. Sinha and S. Banerjee, "Tensile Properties of Zr-2.5Nb Pressure Tube Alloy Between 25 and 800 C," Bhabha Atomic Research Centre, Mumbai, India, 2000.
- [105] K. J. Geelhood, C. E. Beyer and W. G. Luscher, "PNNL Stress/Strain Correlation for Zircaloy," United States Department of Energy, 2008.
- [106] A. Einstein, „On the movement of small particles suspended in a stationary liquid demanded by the molecular-kinetic theory of heat," Bd. 322, Nr. 8, pp. 549-560, 1905.
- [107] H. Magnusson and F. Karin, "Thermodynamic evaluation of the copper-rich part of the Cu-H-O-S-P system at low temperatures," vol. 47, pp. 148-160, 2014.

- [108] M. Ma, W. Xiang, B. Tang, L. Liang, L. Wang and X. Tan, "Non-isothermal and isothermal hydrogen desorption kinetics of zirconium hydride," vol. 467, no. 1, pp. 349-356, 2015.
- [109] M. Ma, L. Liang, B. Tang, W. Xiang, Y. Wang, Y. Cheng and X. Tan, "Decomposition kinetics study of zirconium hydride by interrupted thermal desorption spectroscopy," vol. 645, no. 1, pp. 217-220, 2015.
- [110] E. Zuzek and J. P. Abriata, "The H-Zr (Hydrogen-Zirconium) System," vol. 11, no. 4, 1990.
- [111] W. M. Mueller, J. P. Blackledge and G. G. Libowitz, "Zirconium Hydrides and Hafnium Hydrides," in *Metal Hydrides*, Academic Press, 1968.
- [112] T. B. Douglas, "The Zirconium-Hydrogen System: Some Thermodynamic Properties from a Heat Content Study," *Journal of the American Chemical Society*, vol. 80, no. 19, p. 5040-5046, 1958.
- [113] R. K. Edwards, P. Levesque and D. Cubicciotti, "Solid Solution Equilibria in the Zirconium-Hydrogen System.pdf," vol. 77, no. 5, 1955.
- [114] R. L. Beck, "Zirconium-Hydrogen Phase System," vol. 55, pp. 542-555, 1962.

Appendices

A. Sample Preparation Procedure

The following procedure was adapted from the original [49] with major design changes.

1. **Metal sheets are sectioned using a punching method equipped with a custom die made from hardened dowels to produce circular discs. Use latex gloves whenever handling the materials. Punch the exposed metal surface rather than through the surface covered with a protective coating.** The current configuration uses copper as a barrier so that hydrogen does not enter or leave the system during experimentation.

- a. 2 x LOHC Copper: $\frac{1}{2}$ inch $\varnothing$ x $\frac{1}{32}$ inch thickness
- b. 1 x Zircaloy-2: $\frac{3}{8}$ inch $\varnothing$ x $\frac{3}{64}$ inch thickness

The die (dowel) does not possess a centring guide which prevents undesirable deformation of the sample. The design has been developed for the following reasons:

- a. Surface area is precise and repeatable so that estimating the applied stress on the metal surface is comparatively simple than a square shape
- b. Preparation time is minimised because it avoids machining processes
- c. Circular geometry is commonly studied in theory
- d. An area occupying the Materials Testing Machine is minimal which increases the capacity of experiments that can be done simultaneously

2. **Contact the technical staff in the Civil Laboratory ahead of schedule to arrange training and time on the Materials Testing Machine.** A safety training course is required before handling any equipment.
3. **On the day of the experiment, remove the plastic protective layer from the copper discs.** This layer remains on to prevent excessive buildup of oxides on the surface. Use this surface as the interface between the zirconium disc and the zirconium hydride powder.
4. **If necessary, GOJO® Orange Pumice can help remove grease and other contaminants which accumulate from excessive handling. Wash with cold tap water with every treatment.**
5. **All surfaces (including the perimeters) of the test pieces are roughed by hand with 80 size diamond grit paper to promote a non-bias surface and smooth the surfaces.** Hence, hydrogen will not preferentially migrate towards a surface defect unique to the sample. This step is performed for consistency rather than necessity. Abrasive debris from this step are not expected to interfere with the experimental results.

6. **Samples are then treated with glacial acetic acid (see WHMIS classification) for approximately 30 seconds in a well-ventilated fume hood before being rinsing with cold tap water and quickly dried with Kimwipes™ from KIMTECH Science® or paper towels.** Hot tap water will partially reverse steps 3 to 5. A fume hood was available in the Environment Engineering Laboratory. * Some gloves may not protect against acids. Rubbing edges may damage gloves. Always pour acid into water when mixing *
7. **Allow moisture on the materials to dry so that the precision weighing balance can properly measure the masses.** If the masses change significantly during weighing, then there has not been sufficient dry time. Water will react with the ZrH_2 thereby interfering with the results [66].
8. **Level the analytical balance (Acculab ALC-210.4) with the front feet.** The balance must be calibrated to achieve accuracy. See operating manual for details.

9. **Start by measuring both the copper plates with an analytical balance, then tare the scale, followed by weighing the zirconium disc.** Use a balance with a precision greater than 0.0001 grams or scale the design to be within measuring capability of the zirconium hydride powder.
10. **The diameters and thicknesses of each material are recorded with a high precision digital calliper or a micrometre.** Diameters are used to estimate the applied stress. A comparison between thickness before and after can indicate the level of deformation of the discs. Copper will yield well before zirconium. Knowing how the copper displaces radially at any given temperature and load is used to estimate the minimum distance required to avoid test assemblies from interacting. A graph of yield strength as a function of temperature for copper is also valuable.
11. **Assign the two copper plates and a zirconium disc to an envelope so that the mass of each material is known.** Label each envelope with a letter indicating the clock-wise position it will occupy on the MTS platform and record the weights of the materials used. The date on the envelope is the starting period of the experiment.

Example:

(A)

Cu: 1.8108 g,

Zr: 0.3934 g,

ZrH₂:

2018-01-23

12. **To improve traceability, stamp the same letter found on the envelope on each of the copper discs.** It is important to stamp the surface of the copper plate which will face outward in the assembly. If this is not done properly, zirconium hydride powder will be embedded into the copper surface and may never participate in the experiment.
13. **Mark the perimeter of the zirconium disc with a pointed chisel so that each disc has an affiliation.** When the samples are water quenched in the same container, these features become essential for identification.
14. **Based on the initial information, estimate the desired amount of zirconium hydride powder needed for each assembly with the predictive model.** Otherwise, guess an amount based on experience.

15. **Record the estimate on the envelope at the bottom left corner so that it is not confused with the actual amount.** This calculation acts as a target until the mass of the zirconium is known.

Example:

(A)

Cu: 1.8108 g,

Zr: 0.3934 g,

ZrH₂:

2018-01-23

(0.0065 g)

16. **Repeat step 8 to confirm the recorded masses.** These numbers will be averaged later for measurement accuracy.

Example:

(A)

Cu: 1.8108 g, 1.8108 g

Zr: 0.3934 g, 0.3935 g

ZrH₂:

2018-01-23

(0.0065 g)

17. **Rearrange the discs so that zirconium hydride powder can be piled without being disturbed. Place the copper plates adjacently in the centre of the weighing pan and then stack the zirconium disc on either of the copper plates.** Stacking ensures that the zirconium hydride powder is well within the measurement range of the scale. Both sides of the zirconium disc may have zirconium hydride powder. The time to reach equilibrium is faster if both sides are covered and larger quantities of powder are possible without jeopardising the copper seal.
18. **Tare the balance and begin adding zirconium hydride powder to the centre of the zirconium disc with a spatula. Do not attempt to distribute the powder at this time.** Measurement is time-consuming and requires experience to achieve a target amount. A spatula can be obtained at the campus science store. The stacking method is superior to a beaker method because there are no zirconium hydride losses.

19. Once the mass of zirconium hydride is within the target, remember to clean the tweezers before picking up the copper from the weighing pan and turning it over on top of the zirconium hydride. Beginning at the centre of the copper plate, gently apply downward forces to the assembly to settle the powder so that it spreads across the surface of the zirconium disc. This will flatten the powder slightly. Do not allow the powder to fall from the edge otherwise, account for the loss.
20. Ensure that the hydraulic pump and the MTS-810 load frame are powdered on. Afterwards, secure the M42 super high-speed steel platens in the hydraulic grips. The square thermal shield with a 2" hole in the centre must be positioned between the upper grip of the load frame and the oven. This step must be completed before moving each test assembly. The technical staff are responsible for safety and equipment in the laboratory. Contact them before attempting anything. Grip strength is adjusted on the main console. The thermal shield prevents the convective heat from contacting the hydraulic grip and the load cell. A thermal couple connected to the Thermal Control Unit (TCU) monitors the grips to prevent it from reaching 85 °C.
21. Use the hollow M42 super high-speed steel spacers for the test assembly platform. By stacking two on top of the platen, thermocouples can be inserted into position without being crushed under the MTS load while remaining in the exact proximity of the experiment (Figure 8). Both thermocouples should be together along the axis of the hollow spacers, and the probes should be at the same level as the test assemblies. Make note that a thermal lag between the oven temperature and the experimental setup will occur causing a thermal oscillation. This behaviour can be prevented but does not appear to impact the results of the experiments provided that the oscillation frequency is high, and the amplitude is within reason. See August 29, 2017 and August 30, 2017 experiments in Appendix F as examples.
22. On cleaning the spatula and the tweezers, open the two doors of the analytical scale so that the assembly is accessible to both hands. Each tool is assigned to a hand to manipulate the test assembly. The spatula pushes the assembly to the edge of the weighing pan whereas the tweezer hand receives the payload. It is useful to move the assembly slightly off the edge so that the tweezers can take hold.

23. **Without letting go, transfer the assembly to the materials testing laboratory with an envelope for protection from the elements.** Use an indoor route rather than going outside the buildings. Keep the assemblies upright. Acquire vice grips in the absence of tweezers. The cumbersome tool tends to bend the copper which may cause hydrogen seepage or oxygen contamination. They are also difficult to unclamp if the grips have not been set up correctly.
24. **After the assembly is placed into position, on top of the hollow spacers, check the envelope for signs of zirconium hydride powder.** If there are traces of powder, the assembly has failed to be secured. Repeat the previous steps for the failed assembly, starting at step 4.

B. Materials Testing Procedure

The following assumes that Step 20 from the Sample Preparation Procedure A (Appendix A) has been completed.

1. **Arrange test assemblies in a symmetrical clock-wise fashion according to the envelope labels. Using one hand as a guide and the other as a stabiliser, push the bottom copper disc of each assembly with tweezers or a thin plate material into position.** Make an effort to avoid disturbing the zirconium hydride powder. Symmetry will distribute the applied load evenly to each test assembly. To conduct a comparative stress ($\sigma_i = \vec{F} \div A_i$) study, different sized zirconium discs can be employed on the surface.
2. **Before running the Materials Testing Machine software, determine whether there is sufficient clearance for the oven to close and that the thermocouples are aligned to protrude out of the clamshell oven doors.** The MTS load frame can be manually adjusted with the controls on the main console. * Oven heating coils should never contact metal *
3. **Set the compressive force with the computer software to 1 kN. The rate at which the compressive force is applied should be set to 10 kN per second, and the rate at which it is relieved should be 20 kN per second. Make note that the applied load must reach its target of 1 kN before continuing to any other magnitude. The displacement and force should be recorded for every second until the end of the test to verify the correct conditions have been applied. Results can be named chronologically for analysis.** Recall that the applied stress is a function of both area and force. The compressive force is a negative quantity whereas a tensile force is positive. Ideally, the sum of all surface areas in contact with the load is considered to estimate the applied stress.
4. **Connect the two thermocouples to the monitoring equipment already inserted into the hollow spacers.** See Step 21 from the Sample Preparation Procedure A in the Appendices. One of these is for the TCU which controls the clamshell oven and the other records the temperature over the experimental timespan. Although the TCU is capable of logging the oven temperature, the EL-USB-TC-LCD USB Thermocouple Data Logger is preferred because it has an independent power supply. In the event of a power interruption, the exact time which the experiment trips can be determined. To prevent knocking the experiment off the platen, do not connect thermocouples before applying the compressive load.

5. **Close the oven doors and secure it with the latch.** The two thermocouples should fit between the door crease as described previously.
6. **Place the half-shell heat shields around the top hole of the oven to prevent the heat from escaping vertically.** This step is important because a severe thermal gradient will add variability to the experiment and risk damaging the Materials Testing Machine.
7. **Now that the experimental setup is established, apply the compressive load to the target force.** There is no need for both the top and bottom copper plates to contact each other for the experiment to be successful. The buildup of an extremal oxide layer prevents hydrogen from escaping [46] the system as heat is applied. Under a reducing environment, zirconium absorbs oxides from the metal interface allowing hydrogen to move freely within the system. Zirconium hydride powder dissociates at elevated temperatures.
8. **Before turning on the oven, ensure that the thermocouples are placed in the appropriate monitoring positions for the TCU.** A thermocouple connected to the DP1001AM scanner (right side of the TCU) should be placed at:
 - a. Upper hydraulic grip
 - b. Load cell
 - c. Top hole of the oven
 - d. Upper hydraulic lines
9. **Power on the TCU by toggling the switch on the side of the box. The emergency "stop" button must be depressed at this time.** The CN7223 (left) controller will automatically power, whereas the DP1001AM (right) thermocouple scanner must be manually enabled from the interface. When the device is ready, check that the thermocouple type selected is the same as the type being used for the experiment. * Do not tamper with any of the settings unless the manuals have been well understood!
*
10. **Set the desired operating temperature with the ↑ and ↓ arrows on the CN7223 (left) interface.** The TCU will not adjust for the new temperature unless the return button has been pushed and the red numbers are solid.
11. **Perform a final check to ensure that the experiment will operate as intended.**
12. **Depress the emergency "stop" button with a twisting motion on the TCU to begin the heating processes.** Periodically check on the experiment after it starts to make sure that the conditions are on target.

13. **Ready a bucket of cold tap water taken from within the Civil Laboratory.** Water should be free of contaminants that may interfere with the final results. The bucket will likely be made of plastic. Place a heat-resistant material on the bottom surface of the bucket, so the hot metal does not melt through the bottom while quenching.
14. **When sufficient time has elapsed to reach equilibrium (while the heating and compression conditions have been adequately applied), press the emergency stop button on the TCU so that the current temperature can be monitored while the oven slowly cools to room temperature.** Try to keep the thermocouples in place while performing the following steps.
15. **While the oven still surrounds the experimental setup, disengage the MTS through the computer software and wait for the bottom platen to retract.** This prevents the experiment from cooling over the time needed to remove the material for water quenching.
16. **Open the oven with metal rods or a pair of heat resistant gloves and quickly remove the test assemblies. All metals should be quenched as soon as possible to prevent oxide buildup. A chisel is valuable when metal is stuck together, and tweezers are effective at picking up hot metal in hard to reach places.** Oftentimes, the copper sticks to the roof of the platen. It is more important to quench the zirconium rather than the copper. However, if both metals are quenched fast enough, then their inner surfaces will not be exposed to high-temperature oxidation. Preserving the surfaces is advantageous for future analysis. Gloves can be purchased at the campus science store. * If the gloves become wet, they will be rendered ineffective *
17. **Spacers must be removed from the water before they cool to room temperature and stored safely.** The excess heat evaporates the moisture on the M42 super high-speed steel so that they do not corrode. * Do not leave the hot metal where people commonly travel or where there are flammables. *
18. **While wearing latex gloves, collect the assembly pieces. If any remain attached together, simply apply hand pressure to break them apart. Otherwise, wedge them apart with a chisel or gently tap with a ball peen hammer.** * Do not damage these pieces *
19. **Dry the metals with paper towels and then place them into their respective envelopes for further study later.** By now, each metal should be assigned a letter and a marker to identify where they belong. This is essential for data management.

20. **Retrieve the data from the Thermal Logger and the MTS log file.** Force, displacement, and temperature at each time interval can be aligned and managed with Microsoft© Excel or SYSTAT© SigmaPlot for inspection.

C. Annealing Procedure

When residual hydrides remain on the surface of the zirconium discs, they interfere with the hydrogen analysis which assumes that the hydrogen has penetrated the bulk of the metal. For this reason, an annealing process is necessary to liberate the partially decomposed zirconium hydrides from the surface of the material. Other reasons for annealing the samples are to allow for the hydrogen to become homogenous throughout the material. This process also improves the accuracy of the measurement. As a comparison, McMinns' [17] samples were homogenised at 400 °C for 48 hours after removing surface hydride layers by grinding. They also electrolytically deposited hydrogen into much larger samples which required longer diffusion times.

- A. **Set the ThermoFisher Scientific® Thermolyne™ Benchtop Muffle Furnace to 500 °C by toggling the power switch and holding the "↑" and "↓" buttons to sweep through the temperature range.** Typically, the oven will take half an hour to reach this temperature.
- B. **Sort each envelope associated with the experiment. Apply the same scheme to the order that the zirconium discs will be placed on the furnace tray.** * Do not place the samples directly on the furnace insulation or they will be difficult to retrieve *
- C. **When the oven has reached the target temperature, open the oven doors and place the tray along with the samples into the oven as efficiently as possible to maintain heat.**
- D. **Set a timer for 2 hours.** This time is a sufficient annealing time and is commonly used for experiments. An exact time can be estimated from classical diffusion models.
- E. **When ready, turn off the oven and rest the tray on the oven door with tongs.** Samples need to be cooled gradually.

D. Analysis by Differential Scanning Calorimetry

Refer to the "Operating Instructions DSC 404 C Pegasus" manual.

Specific Instructions:

- Calibrate the machine before beginning an analysis campaign
- Establish a baseline using the following information:

Sample Holder:	6.235.4-63.9.00+S (high accuracy)
Sample type:	Zircaloy-2 (α -phase)
Heating/Cooling Rate:	10 °C / minute (ideal)
Temperature Range:	maximum 550 °C for α -Zr
Number of Cycles:	3 or more

Suggestions and Comments:

- McMinn [17] suggests using a slow-speed cutting wheel in order to minimise heating and cold working the specimen; both affect the Terminal Solid Solubility (TSS). Although these suggestions may be true, a circle punch was used in this study to minimise the specimen size variance. Cold working may only affect the first heating and cooling run. Assume that the possible interference has been annealed on the second and third run.
- α -Zr must not be exposed to 550 °C for an extended period. This eutectic temperature will transform the metal into a new phase and effectively destroy the material. Hydrogen solubility in β -Zr is known to absorb a greater amount of hydrogen than α -Zr.
- The smoothing algorithm for analysis is based on the following sources of mathematics:
 - S.Stearns, D.Hush. Suppressed Golay Savitzky Algorithm taken from: 'Digitale Verarbeitung analoger Signale'. Oldenbourg Verlag München.
 - Abraham Savitzky & Marcel J.E. Golay in Analytical Chemistry, Vol 36, No.8, July 1964, Pages 1627-1638
- Typically, all temperature measurements are usable, with the exception of the first heating run. This is because the first heating run has not experienced the same prior heating and cooling history (10 °C / min).

- The second and third Maximum Slopes of either TSSD or TSSP are compared to determine whether the metal is homogeneous. If there are significant differences, then the samples must be analysed again. Depending on the magnitude, the sample may need to be annealed in an oven as described in Appendix C.
- It is preferable to use samples shaped in a way that thermal contact to the pan is maximised (most samples are disc-shaped) with a mass ranging between 10 and 100 mg [54]. This study found that samples having a mass of 180 mg gave the most repeatable results. This may also be the reason why the CNL chose to use samples of the same mass.

F. Overview of Hydrogen in the System

The following graphs show dashed lines that correspond to the EMCC model (left) and the 1:1 slope (right). The dotted lines are regressions of the data in the figure.

Figure 19 - Stoichiometric relationship and mass balance accountability at 200 °C

Figure 20 - Stoichiometric relationship and mass balance accountability at 250 °C

Figure 21 - Stoichiometric relationship and mass balance accountability at 280 °C

Figure 22 - Stoichiometric relationship and mass balance accountability at 300 °C

Figure 23 - Stoichiometric relationship and mass balance accountability at 350 °C

Figure 24 - Mass balance accountability at 425 °C and 450 °C

Figure 25 - Overview of TSS region for the Zr-H system with the EMCC Model

G. Experimental Outliers

On removal of experimental outliers, an empirically-based model was capable of predicting the behaviour of the observed hydrogen found in the residual zirconium hydride by means of linear regression.

Past Experiments

- CU-LT (320 °C) and Sat-1 (500 °C) experiments have been removed.
 - The CU-LT observation of 73.9 ppm was above the TSS and could not have been predicted with the below TSS model.
 - Sat-1 was inadequately analysed with the DSC at the time and is no longer retrievable.

Current Experiments

Duration

- Hydrides in zirconium appear to require a timescale on the order of hours to reach equilibrium during phase transformations [42].
- Although some samples have been successful after 3 experimental hours, it is recommended to run experiments longer than 20 hours.
 - Discarded: 2017-06-02, 2017-06-12

Pressure

- For these experiments to be predictable, the applied compressive stress of the system should be well above 60 MPa. It is recommended to apply a load well above the yield stress of the grade of copper selected at the experimental temperature. Pressure guarantees that the copper forms a complete seal around the zirconium hydride powder.
- If the inner surfaces are exposed to oxygen, the mechanical hydriding technique is compromised.
- A high-pressure condition also provides a driving force for the hydrogen gas to migrate into the metals quickly. The excessive applied load can also have negative impacts on the performance of mechanical hydriding technique because dislocations appear in both the copper [58] and the zirconium metals which act as hydrogen traps [17].
 - Discarded: 2017-02-16, 2017-03-03, 2017-05-29, 2017-06-12

Copper Grades

- At the beginning of this research project, copper C122 was purchased from Metal Supermarkets Ottawa which was sold as copper C110. This delayed experimentation considerably because the prediction was incompatible with previous observations made by the Differential Scanning Calorimeter (DSC). The hydrogen content predicted with the previous Sieverts constants [49] deviated as much as 65 ppm. A question also arises of whether significant deformation accommodates more hydrogen in the metal. Thin material appears to be more predictable.
 - Discarded: 2016-06-07, 2016-07-20

Sample Preparation

- Occasionally, hydrides embedded themselves on the zirconium metal surface and were difficult to remove without impacting the experimental outcome. Tests were deliberately established to determine if residual surface hydrides would impact the observed concentration. It has been determined that they do.
- Other experiments suffered surface damage caused by a centring pin on the die used to section the zirconium discs. This caused hydrides to attach to the surface and superficially increase observed temperatures made by Differential Scanning Calorimetry (DSC). It was possible to recover a portion of the experiments for DSC analysis by avoiding the centre, where the damage was done. However, this had its own consequences; the hydrogen concentration in the transverse direction is not as uniform as through thickness.

E. Pegasus DSC 404 C Results from Curtis St. Louis Thesis

Figure 26 - MH-1 DSC - 176.0 mg specimen - TSSD MS 319.3 °C

Figure 27 - MH-1 DSC - 176.0 mg specimen - TSSP MS 244.2 °C

Figure 28 - MH-2 DSC - 176.0 mg specimen - TSSD MS 329.7 °C

Figure 29 - MH-2 DSC - 176.0 mg specimen - TSSP MS 254.1 °C

Figure 30 - MH-3 DSC - 185.8 mg specimen - TSSD MS 325.4 °C

Figure 31 - MH-3 DSC - 185.8 mg specimen - TSSP MS 251.3 °C

Figure 32 - CU-LT DSC - 94.5 mg specimen - TSSD MS 344.0 °C

Figure 33 - CU-LT DSC - 94.5 mg specimen - TSSP MS 270.7 °C

Figure 34 - CU-50 DSC - 180.8 mg specimen - TSSD MS 268.4 °C

Figure 35 - CU-50 DSC - 180.8 mg specimen - TSSP MS 189.3 °C

Figure 36 - CU-100 DSC - 178.2 mg specimen - TSSD MS 268.1 °C

Figure 37 - CU-100 DSC - 178.2 mg specimen - TSSP MS 188.3 °C

Figure 38 - SAT-1 DSC - 119.3 mg specimen - TSSD MS 498.5 °C

Figure 39 - SAT-1 DSC - 119.3 mg specimen - TSSP MS 188.3 °C

Figure 40 - SAT-2Bottom DSC - 147.1 mg specimen - TSSD MS 359.4 °C

Figure 41 - SAT-2Bottom DSC - 147.1 mg specimen - TSSP MS 287.1 °C

Figure 42 - SAT-2Middle DSC - 160.9 mg specimen - TSSD MS 361.9 °C

Figure 43 - SAT-2Middle DSC - 160.9 mg specimen - TSSP MS 291.0 °C

Figure 44 - SAT-2Top DSC - 146.0 mg specimen - TSSD MS 395.6 °C

Figure 45 - SAT-2Top DSC - 146.0 mg specimen - TSSP MS 326.5 °C

Figure 46 - SAT-3Bottom DSC - 136.8 mg and 138.2 mg specimens - TSSD MS 408.3 °C

Figure 47 - SAT-3Bottom DSC - 136.8 mg and 138.2 mg specimens - TSSP MS 342.1 °C

Figure 48 - SAT-3Middle DSC - 124.2 mg specimen - TSSD MS 434.2 °C

Figure 49 - SAT-3Middle DSC - 124.2 mg specimen - TSSP MS 372.7 °C

Figure 50 - SAT-3Top DSC - 155.0 mg specimen - TSSD MS 371.3 °C

Figure 51 - SAT-3Top DSC - 155.0 mg specimen - TSSP MS 298.5 °C

F.MTS 810 Test System & Pegasus DSC 404 C Results

Figure 52 - Jun 07, 2016 MTS - 189.964 ± 0.014 kN at 352.5 ± 0.4 °C for 8375 min

- Thermometer turned off at 6 AM June 13 because it ran out of memory

Figure 53 - Jun 07, 2016 DSC - 54.9 mg specimen - TSSD MS 405.1 °C

Figure 54 - Jun 07, 2016 DSC - 54.9 mg specimen - TSSP MS 341.1 °C

Figure 55 - Jun 07, 2016 DSC - 78.7 mg specimen - TSSD MS 438.5 °C

Figure 56 - Jun 07, 2016 DSC - 78.7 mg specimen - TSSP MS 377.6 °C

Figure 57 - Jun 07, 2016 DSC - 46.3 mg specimen - TSSD MS 450.0 °C

Figure 58 - Jun 07, 2016 DSC - 46.3 mg specimen - TSSP MS 383.8 °C

Figure 59 - Jul 04, 2016 MTS - 95.554 ± 0.015 kN at 353.3 ± 7.2 °C for 9950 min

Figure 60 - Jul 13, 2016 MTS - 117.457 ± 0.014 kN at 435.3 ± 0.4 °C for 7130 min

- Combined with another experiment in a stack
- C122 was used

Figure 61 - Jul 13, 2016 DSC - 38.2 mg and 75.8 mg specimens - TSSD MS 425.9 °C

Figure 62 - Jul 13, 2016 DSC - 38.2 mg and 75.8 mg specimens - TSSP MS 361.0 °C

Figure 63 - Jul 20, 2016 MTS - 95.934 ± 0.010 kN at 364.2 ± 0.4 °C for 8350 min

Figure 64 - Jul 20, 2016 DSC - 56.8 mg specimen - TSSD MS 373.9 °C

Figure 65 - Jul 20, 2016 DSC - 56.8 mg specimen - TSSP MS 303.4 °C

Figure 66 - Jul 20, 2016 DSC - 44.8 mg specimen - TSSD MS 382.7 °C

Figure 67 - Jul 20, 2016 DSC - 44.8 mg specimen - TSSP MS 313.3 °C

Figure 68 - Jul 20, 2016 DSC - 54.8 mg specimen - TSSD MS 443.4 °C

Figure 69 - Jul 20, 2016 DSC - 54.8 mg specimen - TSSP MS 380.4 °C

Figure 70 - Aug 02, 2016 MTS - 89.010 ± 0.009 kN at 350.6 ± 1.7 °C for 8520 min

Figure 71 - Aug 02, 2016 DSC - 100.3 mg specimen - TSSD MS 422.5 °C

Figure 72 - Aug 02, 2016 DSC - 100.3 mg specimen - TSSP MS 355.0 °C

Figure 73 - Aug 15, 2016 MTS - 115.009 ± 0.010 kN at 347.3 ± 5.5 °C for 9995 min

- Still attached to the copper when annealed

Figure 74 - Oct 06, 2016 MTS - 17.324 ± 0.011 kN at 336.9 ± 0.3 °C for 8575 min

Figure 75 - Oct 06, 2016 DSC Analysis - 82.6 mg specimen - TSSD MS 336.6 °C

Figure 76 - Oct 06, 2016 DSC - 82.6 mg specimen - TSSP MS 261.1 °C

Figure 77 - Oct 06, 2016 DSC - 72.0 mg specimen - TSSD MS 383.2 °C

Figure 78 - Oct 06, 2016 DSC - 72.0 mg specimen - TSSP MS 313.7 °C

Figure 79 - Oct 26, 2016 MTS - 17.170 ± 0.009 kN at 355.7 ± 0.7 °C for 8545 min

Figure 80 - Oct 26, 2016 DSC - 80.9 mg specimen - TSSD MS 311.6 °C

Figure 81 - Oct 26, 2016 DSC - 80.9 mg specimen - TSSP MS 233.9 °C

Figure 82 - Oct 26, 2016 DSC - 81.5 mg specimen - TSSD MS 378.2 °C

Figure 83 - Oct 26, 2016 DSC - 81.5 mg specimen - TSSP MS 308.4 °C

Figure 84 - Jan 19, 2017 MTS - 54.026 ± 0.011 kN at 352.6 ± 0.4 °C for 8335 min

- Three sample setup on a single layer

Figure 85 - Jan 19, 2017 DSC - 54.2 mg specimen - TSSD MS 338.8 °C

Figure 86 - Jan 19, 2017 DSC - 54.2 mg specimen - TSSP MS 264.6 °C

Figure 87 - Jan 19, 2017 DSC - 69.2 mg specimen - TSSD MS 416.7 °C

Figure 88 - Jan 19, 2017 DSC - 69.2 mg specimen - TSSP MS 348.9 °C

Figure 89 - Jan 19, 2017 DSC - 76.2 mg specimen - TSSD MS 468.3 °C

Figure 90 - Jan 19, 2017 DSC - 76.2 mg specimen - TSSP MS 407.6 °C

Figure 91 - Feb 02, 2017 MTS - 71.728 ± 0.013 kN at 355.0 ± 2.0 °C for 8555 min

Figure 92 - Feb 02, 2017 DSC - 81.1 mg specimen - TSSD MS 375.1 °C

Figure 93 - Feb 02, 2017 DSC - 81.1 mg specimen - TSSP MS 305.9 °C

Figure 94 - Feb 02, 2017 DSC - 82.4 mg specimen - TSSD MS 382.2 °C

Figure 95 - Feb 02, 2017 DSC - 82.4 mg specimen - TSSP MS 311.2 °C

Figure 96 - Feb 02, 2017 DSC - 76.0 mg specimen - TSSD MS 426.4 °C

Figure 97 - Feb 02, 2017 DSC - 76.0 mg specimen - TSSP MS 361.5 °C

Figure 98 - Feb 02, 2017 DSC - 90.8 mg specimen - TSSD MS 515.8 °C

Figure 99 - Feb 02, 2017 DSC - 90.8 mg specimen - TSSP MS 454.3 °C

Figure 100 - Feb 15, 2017 MTS - 18.762 ± 0.008 kN at 343.1 ± 1.1 °C for 1150 min

Figure 101 - Feb 15, 2017 DSC - 53.5 mg specimen - TSSD MS 312.3 °C

Figure 102 - Feb 15, 2017 DSC - 53.5 mg specimen - TSSP MS 235.5 °C

Figure 103 - Feb 15, 2017 DSC - 62.0 mg specimen - TSSD MS 399.1 °C

Figure 104 - Feb 15, 2017 DSC - 62.0 mg specimen - TSSP MS 330.6 °C

Figure 105 - Feb 15, 2017 DSC - 64.0 mg specimen - TSSD MS 423.7 °C

Figure 106 - Feb 15, 2017 DSC - 64.0 mg specimen - TSSP MS 357.6 °C

Figure 107 - Feb 16, 2017 MTS - 18.431 ± 0.010 kN at 366.8 ± 1.2 °C for 6995 min

Figure 108 - Feb 16, 2017 DSC - 101.1 mg specimen - TSSD MS 302.4 °C

Figure 109 - Feb 16, 2017 DSC - 101.1 mg specimen - TSSP MS 225.7 °C

Figure 110 - Feb 16, 2017 DSC - 100.7 mg specimen - TSSD MS 374.0 °C

Figure 111 - Feb 16, 2017 DSC - 100.7 mg specimen - TSSP MS 303.9 °C

Figure 112 - Feb 16, 2017 DSC - 109.4 mg and 97.0 mg specimens - TSSD MS 409.9 °C

Figure 113 - Feb 16, 2017 DSC - 109.4 mg and 97.0 mg specimens - TSSP MS 342.2 °C

Figure 114 - Mar 03, 2017 MTS - 7.652 ± 0.009 kN at 355.4 ± 3.3 °C for 8360 min

- Disruptions around 3 PM on March 03, 2017 happened after removing the thermocouple
- The oven temperature was unaffected

Figure 115 - Mar 03, 2017 DSC - 75.8 mg specimen - TSSD MS 457.0 °C

Figure 116 - Mar 03, 2017 DSC - 75.8 mg specimen - TSSP MS 389.8 °C

Figure 117 - Apr 12, 2017 MTS - 34.802 ± 0.011 kN at 351.8 ± 3.5 °C for 8410 min

Figure 118 - Apr 12, 2017 DSC - 74.3 mg and 74.9 mg specimens - TSSD MS 318.6 °C

Figure 119 - Apr 12, 2017 DSC - 78.0 mg specimen - TSSD MS 371.2 °C

Figure 120 - Apr 12, 2017 DSC - 78.0 mg specimen - TSSP MS 300.4 °C

Figure 121 - Apr 12, 2017 DSC - 84.8 mg specimen - TSSD MS 377.9 °C

Figure 122 - Apr 12, 2017 DSC - 84.8 mg specimen - TSSP MS 308.0 °C

Figure 123 - Apr 12, 2017 DSC - 81.7 mg specimen - TSSD MS 406.4 °C

Figure 124 - Apr 12, 2017 DSC - 81.7 mg specimen - TSSP MS 338.4 °C

Figure 125 - May 29, 2017 MTS - 3.129 ± 0.114 kN at 300.7 ± 4.9 °C for 1180 min

Figure 126 - May 29, 2017 DSC - 83.2 mg specimen - TSSD MS 234.4 °C

Figure 127 - May 29, 2017 DSC - 83.2 mg specimen - TSSP MS 151.0 °C

Figure 128 - May 29, 2017 DSC - 81.6 mg specimen - TSSD MS 267.8 °C

Figure 129 - May 29, 2017 DSC - 81.6 mg specimen - TSSP MS 177.9 °C

Figure 130 - May 29, 2017 DSC - 95.2 mg specimen - TSSD MS 288.9 °C

Figure 131 - May 29, 2017 DSC - 95.2 mg specimen - TSSP MS 209.4 °C

Figure 132 - May 29, 2017 DSC - 77.8 mg specimen - TSSD MS 343.3 °C

Figure 133 - May 29, 2017 DSC - 77.8 mg specimen - TSSP MS 268.8 °C

Figure 134 - May 30, 2017 MTS - 41.042 ± 0.009 kN at 301.2 ± 4.8 °C for 1190 min

Figure 135 - May 30, 2017 DSC - 60.3 mg specimen - TSSD MS 290.7 °C

Figure 136 - May 30, 2017 DSC - 60.3 mg specimen - TSSP MS 212.5 °C

Figure 137 - May 30, 2017 DSC - 64.5 mg specimen - TSSD MS 369.2 °C

Figure 138 - May 30, 2017 DSC - 64.5 mg specimen - TSSP MS 297.9 °C

Figure 139 - May 30, 2017 DSC - 64.9 mg specimen - TSSD MS 403.4 °C

Figure 140 - May 30, 2017 DSC - 64.9 mg specimen - TSSP MS 335.0 °C

Figure 141 - May 30, 2017 DSC - 76.9 mg specimen - TSSD MS 430.2 °C

Figure 142 - May 30, 2017 DSC - 76.9 mg specimen - TSSP MS 365.3 °C

Figure 143 - May 31, 2017 MTS - 41.012 ± 0.010 kN at 348.3 ± 3.9 °C for 1190 min

Figure 144 – May 31, 2017 DSC – 57.5 mg specimen – TSSD MS 305.6 °C

Figure 145 – May 31, 2017 DSC – 57.5 mg specimen – TSSP MS 229.0 °C

Figure 146 – May 31, 2017 DSC – 52.1 mg specimen – TSSD MS 386.5 °C

Figure 147 – May 31, 2017 DSC – 52.1 mg specimen – TSSP MS 317.5 °C

Figure 148 - May 31, 2017 DSC - 66.2 mg specimen - TSSD MS 393.6 °C

Figure 149 - May 31, 2017 DSC - 66.2 mg specimen - TSSP MS 326.5 °C

Figure 150 - May 31, 2017 DSC - 65.0 mg specimen - TSSD MS 436.6 °C

Figure 151 - May 31, 2017 DSC - 65.0 mg specimen - TSSP MS 371.9 °C

Figure 152 - Jun 01, 2017 MTS - 34.891 ± 0.009 kN at 299.4 ± 4.0 °C for 1010 min

Figure 153 - Jun 01, 2017 DSC - 44.5 mg specimen - TSSD MS 308.2 °C

Figure 154 - Jun 01, 2017 DSC - 44.5 mg specimen - TSSP MS 232.0 °C

Figure 155 - Jun 01, 2017 DSC - 63.0 mg specimen - TSSD MS 394.0 °C

Figure 156 - Jun 01, 2017 DSC - 63.0 mg specimen - TSSP MS 324.8 °C

Figure 157 - Jun 01, 2017 DSC - 66.0 mg specimen - TSSD MS 395.8 °C

Figure 158 - Jun 01, 2017 DSC - 66.0 mg specimen - TSSP MS 327.9 °C

Figure 159 - Jun 01, 2017 DSC - 53.0 mg specimen - TSSD MS 443.3 °C

Figure 160 - Jun 01, 2017 DSC - 53.0 mg specimen - TSSP MS 378.2 °C

Figure 161 - Jun 02, 2017 MTS - 39.841 ± 0.008 kN at 279.7 ± 5.6 °C for 160 min

Figure 162 - Jun 02, 2017 DSC - 67.9 mg specimen - TSSD MS 315.3 °C

Figure 163 - Jun 02, 2017 DSC - 67.9 mg specimen - TSSP MS 239.2 °C

Figure 164 - Jun 02, 2017 DSC - 63.9 mg specimen - TSSD MS 394.2 °C

Figure 165 - Jun 02, 2017 DSC - 63.9 mg specimen - TSSP MS 327.7 °C

Figure 166 - Jun 02, 2017 DSC - 68.9 mg specimen - TSSD MS 477.2 °C

Figure 167 - Jun 02, 2017 DSC - 68.9 mg specimen - TSSP MS 416.3 °C

Figure 168 - Jun 02, 2017 DSC - 74.2 mg specimen - TSSD MS 508.1 °C

Figure 169 - Jun 02, 2017 DSC - 74.2 mg specimen - TSSP MS 451.4 °C

Figure 170 - Jun 05, 2017 MTS - 39.883 ± 0.010 kN at 281.5 ± 4.9 °C for 1165 min

Figure 171 - Jun 05, 2017 DSC - 64.3 mg specimen - TSSD MS 347.2 °C

Figure 172 - Jun 05, 2017 DSC - 64.3 mg specimen - TSSP MS 273.0 °C

Figure 173 - Jun 05, 2017 DSC - 57.5 mg specimen - TSSD MS 435.1 °C

Figure 174 - Jun 05, 2017 DSC - 57.5 mg specimen - TSSP MS 368.1 °C

Figure 175 - Jun 05, 2017 DSC - 75.4 mg specimen - TSSD MS 473.9 °C

Figure 176 - Jun 05, 2017 DSC - 75.4 mg specimen - TSSP MS 408.9 °C

Figure 177 - Jun 05, 2017 DSC - 82.2 mg specimen - TSSD MS 537.4 °C

Figure 178 - Jun 05, 2017 DSC - 82.2 mg specimen - TSSP MS 490.7 °C

Figure 179 - Jun 06, 2017 MTS - 39.822 ± 0.009 kN at 281.5 ± 4.5 °C for 1310 min

Figure 180 - Jun 06, 2017 DSC - 101.1 mg (unannealed) and 127.4 mg specimens - TSSD MS 328.6 °C

Figure 181 - Jun 06, 2017 DSC - 101.1 mg (unannealed) and 127.4 mg specimens - TSSP MS 251.1 °C

Figure 182 - Jun 06, 2017 DSC - 89.3 mg (unannealed) and 113.2 mg specimens - TSSD MS 438.6 °C

Figure 183 - Jun 06, 2017 DSC - 89.3 mg (unannealed) and 113.2 mg specimens - TSSP MS 373.7 °C

Figure 184 - Jun 12, 2017 MTS - 91.650 ± 0.012 kN at 283.0 ± 6.5 °C for 160 min

Figure 185 - Jun 12, 2017 DSC - 63.3 mg specimen - TSSD MS 452.6 °C

Figure 186 - Jun 12, 2017 DSC - 63.3 mg specimen - TSSP MS 387.3 °C

Figure 187 - Jun 12, 2017 DSC - 77.5 mg specimen - TSSD MS 423.1 °C

Figure 188 - Jun 12, 2017 DSC - 77.5 mg specimen - TSSP MS 357.1 °C

Figure 189 - Jun 12, 2017 DSC - 78.2 mg specimen - TSSD MS 357.3 °C

Figure 190 - Jun 12, 2017 DSC - 78.2 mg specimen - TSSP MS 285.7 °C

Figure 191 - Jun 12, 2017 DSC - 67.2 mg specimen - TSSD MS 435.5 °C

Figure 192 - Jun 12, 2017 DSC - 67.2 mg specimen - TSSP MS 370.2 °C

Figure 193 - Jun 13, 2017 MTS - 22.928 ± 0.008 kN at 281.9 ± 5.9 °C for 160 min

Figure 194 - Jul 12, 2017 MTS - 100.992 ± 0.014 kN at 300.7 ± 3.7 °C for 1445 min

Figure 195 - Jul 14, 2017 MTS - 26.019 ± 0.013 kN at 300.7 ± 2.5 °C for 4075 min

Figure 196 - Jul 19, 2017 MTS - 10.999 ± 0.009 kN at 281.7 ± 2.8 °C for 1330 min

Figure 197 - Jul 31, 2017 MTS - 21.003 ± 0.149 kN at 280.5 ± 1.8 °C for 1370 min

Figure 198 - Aug 21, 2017 MTS - 40.801 ± 0.010 kN at 249.9 ± 3.5 °C for 1095 min

Figure 199 - Aug 21, 2017 DSC - 174.6 mg specimen - TSSD MS 310.4 °C

Figure 200 - Aug 21, 2017 DSC - 174.6 mg specimen - TSSP MS 230.4 °C

Figure 201 - Aug 21, 2017 DSC - 172.1 mg specimen - TSSD MS 375.2 °C

Figure 202 - Aug 21, 2017 DSC - 172.1 mg specimen - TSSP MS 302.6 °C

Figure 203 - Aug 21, 2017 DSC - 176.0 mg specimen - TSSD MS 298.9 °C

Figure 204 - Aug 21, 2017 DSC - 176.0 mg specimen - TSSP MS 218.4 °C

Figure 205 - Aug 21, 2017 DSC - 176.2 mg specimen - TSSD MS 424.8 °C

Figure 206 - Aug 21, 2017 DSC - 176.2 mg specimen - TSSP MS 353.4 °C

Figure 207 - Aug 29, 2017 MTS - 40.843 ± 0.013 kN at 282.0 ± 5.3 °C for 1205 min

Figure 208 - Aug 29, 2017 DSC - 173.6 mg specimen - TSSD MS 362.8 °C

Figure 209 - Aug 29, 2017 DSC - 173.6 mg specimen - TSSP MS 289.0 °C

Figure 210 - Aug 29, 2017 DSC - 170.1 mg specimen - TSSD MS 382.1 °C

Figure 211 - Aug 29, 2017 DSC - 170.1 mg specimen - TSSP MS 310.5 °C

Figure 212 - Aug 29, 2017 DSC - 177.6 mg specimen - TSSD MS 346.7 °C

Figure 213 - Aug 29, 2017 DSC - 177.6 mg specimen - TSSP MS 271.0 °C

Figure 214 - Aug 29, 2017 DSC - 175.2 mg specimen - TSSD MS 407.3 °C

Figure 215 - Aug 29, 2017 DSC - 175.2 mg specimen - TSSP MS 340.4 °C

Figure 216 - Aug 30, 2017 MTS - 40.826 ± 0.011 kN at 275.9 ± 0.2 °C for 1200 min

Figure 217 - Aug 30, 2017 DSC - 173.6 mg specimen - TSSD MS 358.4 °C

Figure 218 - Aug 30, 2017 DSC - 173.6 mg specimen - TSSP MS 283.8 °C

Figure 219 - Aug 30, 2017 DSC - 172.3 mg specimen - TSSD MS 374.0 °C

Figure 220 - Aug 30, 2017 DSC - 172.3 mg specimen - TSSP MS 301.4 °C

Figure 221 - Aug 30, 2017 DSC - 179.1 mg specimen - TSSD MS 345.3 °C

Figure 222 - Aug 30, 2017 DSC - 179.1 mg specimen - TSSP MS 270.7 °C

Figure 223 - Aug 30, 2017 DSC - 174.7 mg specimen - TSSD MS 411.9 °C

Figure 224 - Aug 30, 2017 DSC - 174.7 mg specimen - TSSP MS 342.7 °C

Figure 225 - Sep 05, 2017 MTS - 18.836 ± 0.012 kN at 349.7 ± 4.5 °C for 8380 min

Figure 226 - Sep 05, 2017 DSC - 168.9 mg specimen - TSSD MS 433.9 °C

Figure 227 - Sep 05, 2017 DSC - 168.9 mg specimen - TSSP MS 364.9 °C

Figure 228 - Sep 05, 2017 DSC - 180.6 mg specimen - TSSD MS 353.1 °C

Figure 229 - Sep 05, 2017 DSC - 180.6 mg specimen - TSSP MS 276.8 °C

Figure 230 - Sep 05, 2017 DSC - 178.8 mg specimen - TSSD MS 343.5 °C

Figure 231 - Sep 05, 2017 DSC - 178.8 mg specimen - TSSP MS 267.2 °C

Figure 232 - Sep 05, 2017 DSC - 175.8 mg specimen - TSSD MS 449.4 °C

Figure 233 - Sep 05, 2017 DSC - 175.8 mg specimen - TSSP MS 380.4 °C

Figure 234 - Sep 13, 2017 MTS - 55.864 ± 0.014 kN at 282.1 ± 5.4 °C for 1195 min

Figure 235 - Sep 13, 2017 DSC - 173.9 mg specimen - TSSD MS 329.6 °C

Figure 236 - Sep 13, 2017 DSC - 173.9 mg specimen - TSSP MS 253.9 °C

Figure 237 - Sep 13, 2017 DSC - 164.7 mg specimen - TSSD MS 381.1 °C

Figure 238 - Sep 13, 2017 DSC - 164.7 mg specimen - TSSP MS 310.9 °C

Figure 239 - Sep 13, 2017 DSC - 175.6 mg specimen - TSSD MS 383.0 °C

Figure 240 - Sep 13, 2017 DSC - 175.6 mg specimen - TSSP MS 312.4 °C

Figure 241 - Sep 13, 2017 DSC - 170.3 mg specimen - TSSD MS 418.1 °C

Figure 242 - Sep 13, 2017 DSC - 170.3 mg specimen - TSSP MS 351.6 °C

Figure 243 - Dec 18, 2017 MTS - 40.796 ± 0.043 kN at 255.4 ± 4.8 °C for 1210 min

Figure 244 - Dec 18, 2017 DSC - 174.3 mg specimen - TSSD MS 383.9 °C

Figure 245 - Dec 18, 2017 DSC - 174.3 mg specimen - TSSP MS 314.0 °C

Figure 246 - Dec 18, 2017 DSC - 169.6 mg specimen - TSSD MS 347.6 °C

Figure 247 - Dec 18, 2017 DSC - 169.6 mg specimen - TSSP MS 273.1 °C

Figure 248 - Dec 18, 2017 DSC - 176.7 mg specimen - TSSD MS 332.9 °C

Figure 249 - Dec 18, 2017 DSC - 176.7 mg specimen - TSSP MS 260.9 °C

Figure 250 - Dec 18, 2017 DSC - 177.1 mg specimen - TSSD MS 354.1 °C

Figure 251 - Dec 18, 2017 DSC - 177.1 mg specimen - TSSP MS 282.2 °C

Figure 252 - Dec 19, 2017 MTS - 40.794 ± 0.054 kN at 253.1 ± 3.8 °C for 1190 min

Figure 253 - Dec 19, 2017 DSC - 177.8 mg specimen - TSSD MS 318.2 °C

Figure 254 - Dec 19, 2017 DSC - 177.8 mg specimen - TSSP MS 241.0 °C

Figure 255 - Dec 19, 2017 DSC - 173.9 mg specimen - TSSD MS 352.8 °C

Figure 256 - Dec 19, 2017 DSC - 173.9 mg specimen - TSSP MS 277.9 °C

Figure 257 - Dec 19, 2017 DSC - 176.2 mg specimen - TSSD MS 327.6 °C

Figure 258 - Dec 19, 2017 DSC - 176.2 mg specimen - TSSP MS 250.8 °C

Figure 259 - Dec 19, 2017 DSC - 175.4 mg specimen - TSSD MS 344.3 °C

Figure 260 - Dec 19, 2017 DSC - 175.4 mg specimen - TSSP MS 271.0 °C

Figure 261 - Jan 10, 2018 MTS - 81.600 ± 0.019 kN at 201.5 ± 4.0 °C for 1335 min

- The hydraulic pump disengaged as a result of an electrical trip.

Figure 262 - Jan 10, 2018 DSC - 173.8 mg specimen - TSSD MS 311.3 °C

Figure 263 - Jan 10, 2018 DSC - 173.8 mg specimen - TSSP MS 234.0 °C

Figure 264 - Jan 10, 2018 DSC - 174.6 mg specimen - TSSD MS 302.7 °C

Figure 265 - Jan 10, 2018 DSC - 174.6 mg specimen - TSSP MS 223.7 °C

Figure 266 - Jan 10, 2018 DSC - 171.3 mg specimen - TSSD MS 329.6 °C

Figure 267 - Jan 10, 2018 DSC - 171.3 mg specimen - TSSP MS 254.7 °C

Figure 268 - Jan 10, 2018 DSC - 171.9 mg specimen - TSSD MS 349.3 °C

Figure 269 - Jan 10, 2018 DSC - 171.9 mg specimen - TSSP MS 272.7 °C

Figure 270 - Jan 23, 2018 MTS - 142.799 ± 0.033 kN at 204.2 ± 4.6 °C for 1335 min

Figure 271 - Jan 23, 2018 DSC - 173.0 mg specimen - TSSD MS 268.8 °C

Figure 272 - Jan 23, 2018 DSC - 173.0 mg specimen - TSSP MS 176.3 °C

Figure 273 - Jan 23, 2018 DSC - 173.4 mg specimen - TSSD MS 268.9 °C

Figure 274 - Jan 23, 2018 DSC - 173.4 mg specimen - TSSP MS 177.3 °C

Figure 275 - Jan 23, 2018 DSC - 172.3 mg specimen - TSSD MS 270.0 °C

Figure 276 - Jan 23, 2018 DSC - 172.3 mg specimen - TSSP MS 186.6 °C

Figure 277 - Jan 23, 2018 DSC - 248.7 mg specimen - TSSD MS 283.7 °C

Figure 278 - Jan 23, 2018 DSC - 248.7 mg specimen - TSSP MS 214.3 °C

Figure 279 - Jan 23, 2018 DSC - 170.3 mg specimen - TSSD MS 291.3 °C

Figure 280 - Jan 23, 2018 DSC - 170.3 mg specimen - TSSP MS 210.7 °C

Figure 281 - Jan 23, 2018 DSC - 172.1 mg specimen - TSSD MS 336.4 °C

Figure 282 - Jan 23, 2018 DSC - 172.1 mg specimen - TSSP MS 263.9 °C