Filling the Gaps in SCWR Materials Research: Advanced Nuclear Corrosion Research Facilities in Hamilton

J. L. Krausher[1], W. Zheng[1], J. Li[1], D. Guzonas[2] and G. Botton[3]

[1]NRCan-CANMET Materials Technology Laboratory, Hamilton, ON
[2]AECL-Chalk River, Chalk River, ON
[3]McMaster University, Hamilton, ON

Abstract

Research efforts on materials selection and development in support of the design of supercritical water-cooled reactors (SCWRs) have produced a considerable amount of data on corrosion, creep and other related properties. Summaries of the data on corrosion [1] and stress corrosion cracking [2] have recently been produced. As research on the SCWR advances, gaps and limitations in the published data are being identified. In terms of corrosion properties, these gaps can be seen in several areas, including: 1) the test environment, 2) the physical and chemical severity of the tests conducted as compared with likely reactor service/operating conditions, and 3) the test methods used. While some of these gaps can be filled readily using existing facilities, others require the availability of advanced test facilities for specific tests and assessments. In this paper, highlights of the new materials research facilities jointly established in Hamilton by CANMET Materials Technology Laboratory and McMaster University are presented.

1. Corrosion research in support of SCWR

Over the past decades, several concepts for a supercritical water cooled reactor (SCWR) have been proposed. Both pressure vessel and pressure-tube SCWR (PT-SCWR) concepts are being explored, involving a large number of researchers from the Generation IV International Forum (GIF) community. In Canada, the PT-SCWR is seen as a logical evolution of current CANDU[1] designs. To achieve high thermal efficiency, the operating temperatures and pressures in the reactor core will be significantly higher (625°C and 25 MPa at the point of coolant exit) than those of existing CANDU and pressurized water reactors (PWRs). These aggressive conditions render most currently used materials unsuitable for use as in-core and some out-of-core components.

Materials research for the SCWR has been underway for many decades, starting in the early 1950s [3,4]. In the recent survey of SCWR-related corrosion test results [5], over 500 data sets have been collected covering over 95 ferritic, austenitic and Ni-based alloys. Figure 1 shows the distribution of the test data between five temperature ranges from 50°C to 732°C. As this database was designed for the SCWR application, only a limited number of results are included for tests in subcritical water. In the supercritical water regime, the majority of the data collected fall in the temperature range from 450°C to 538°C.

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[1] CANDU®, **CAN**ada **D**euterium **U**ranium, is a registered trademark of Atomic Energy of Canada Limited (AECL).

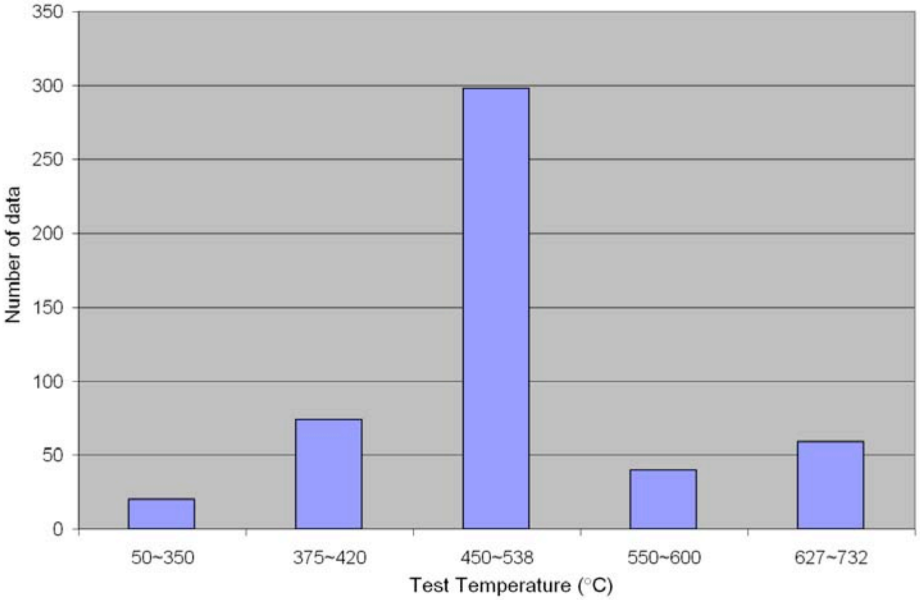

Figure 1: Distribution of the reported test data among five temperature ranges from 50℃ to 732℃.

It is important to note that in most studies, only the coupon weight change after the test is given; this is only a valid measure of the corrosion rate if the total amount of metal released into the test system is insignificant. Unfortunately, in most reported studies, descaling of the coupon to obtain the weight loss or detailed analyses of the fraction of the metal dissolved or lost in the test solution were not included.

2. Gaps in the published data

2.1 General observations

The survey of literature revealed that few experimenters have used exactly the same test conditions (temperature, pressure, test duration, water chemistry), so inter-laboratory comparisons are difficult to make. The influence of water density and chemistry has not adequately been examined. Most tests conducted used pure water under a test pressure of 25 MPa. Typical dissolved oxygen concentrations are either very low (de-aerated water at tens of ppb) or 8~10 ppm. In the corrosion work planned for the future, this gap will be addressed in the overall design of test matrices and especially in the stress corrosion cracking (SCC) tests as the SCC susceptibility of an alloy is strongly dependent on the chemistry of the test solution.

2.2 Test temperature

For most alloys, the measured weight change increases with increasing temperature. This is expected given the general dependence of corrosion kinetics on temperature. However, for some alloy classes, the rate of increase in corrosion rate as the temperature increases above 500℃ is higher than that observed below 500℃. Betova [6] and Zhang [7] have both observed this transition in their respective work. Betova suggested the more rapid oxidation at 600^{o}C over 500℃ is associated with the change in the corrosion mechanism from a high-temperature electrochemical mechanism to a more gas phase (air and water vapour) type of process. In Zhang's study of C-276, the formation of coarser and thicker oxidation products was observed at

550 and 600℃ on the alloy surface. The detailed mechanism(s) for this transition remains to be studied, as a number of chemical and physical properties of water change when the temperature is increased; these include the solubility of the respective oxides, the density and the dielectric constant.

Published data for test temperatures above 650℃ are limited, although some work has been carried out up to at least 760°C by the fossil SCW industry as part of their development effort for ultra-supercritical power plants. There is a serious gap in this regard in terms of the likely operating temperature of the PT-SCWR and the temperature range of the tests conducted. According to the preliminary PT-SCWR design, the surface temperature of fuel claddings could reach as high as 850℃ at some locations of the reactor core. However, the highest stable temperature any existing SCW loop can achieve is about 700℃. Tests using pressurized capsules could in theory be performed up to 850℃, but there is very little control of the water chemistry inside a sealed capsule.

The effects of temperature can also lead to the formation of new phases in the test alloys during testing. For example, heat-resistant stainless steels such as 304, 316 and 310 series as well as NF709 (20%Cr, 25%Ni) can develop various precipitates [8], including the common MX-type precipitate (such as NbC, NbN,TiC, TiN,CrNbN), $M_{23}C_6$, M_6C, the Laves phase (which can form in 316 after 1000 hour aging between 625 and 800°C), the G phase (which form in 20Cr-25Ni in the temperature range of 500 to 850°C) and the sigma (σ) phase. While the $M_{23}C_6$ phase forms readily after a short time (e.g., 30 minutes at 750°C), others require several thousand hours to form. Therefore, long-term testing is needed in order for any possible effects of such precipitates to be revealed.

2.3 Metallurgical conditions of the test alloys

The metallurgical state of a given alloy can have significant effect on the corrosion rate measured in SCW. Tsuchiya et al [9] reported a comparative study of corrosion and SCC properties of normal-size and fine-grain 304L, 316L and 310S stainless steels in SCW of 550°C containing 8 ppm oxygen. In their 6-week long SCW corrosion tests, the corrosion rate of fine-grain alloys was found to be less than 0.005 mm/per year (with the 310S alloy showing a corrosion rate of 0.00017 mm/year) while the alloys with normal grain size (>25 microns) showed corrosion rate of greater than 0.01 mm/year. This could be related to the fact that enhanced Cr diffusion in fine-grained material helps improve the passivation of the alloys in SCW; enhanced passivity would benefit both resistance to stress corrosion and general corrosion. Indeed, their Auger Electron Spectroscopy (AES) analysis showed higher level of Cr in the oxide formed on the fine-grain samples than that in the normal material.

The surface finish of the test samples can play a large role in determining the corrosion rate, as seen in Figure 2. Of the various SCW corrosion data for 304 SS in the survey, the largest variation of corrosion rate data, among all test parameters, was associated with the surface finish [10].

In a recent study of the corrosion rates of 316L in the as-machined and polished condition [11], the machined surface exhibited a corrosion rate that is less than 10% of the polished surface. The corrosion tests ran for 3000 hours (125 days) at 650^{o}C in de-aerated water kept at 25 MPa. Metallurgically the machined surface showed a fine-grained sub-surface layer of several microns in depth. This fine structure was a result of re-crystallization of the cold-worked (by machining) surface layer, and the much improved corrosion resistance is very similar to that observed by Tsuchiya et al [9] on their 3xx alloys.

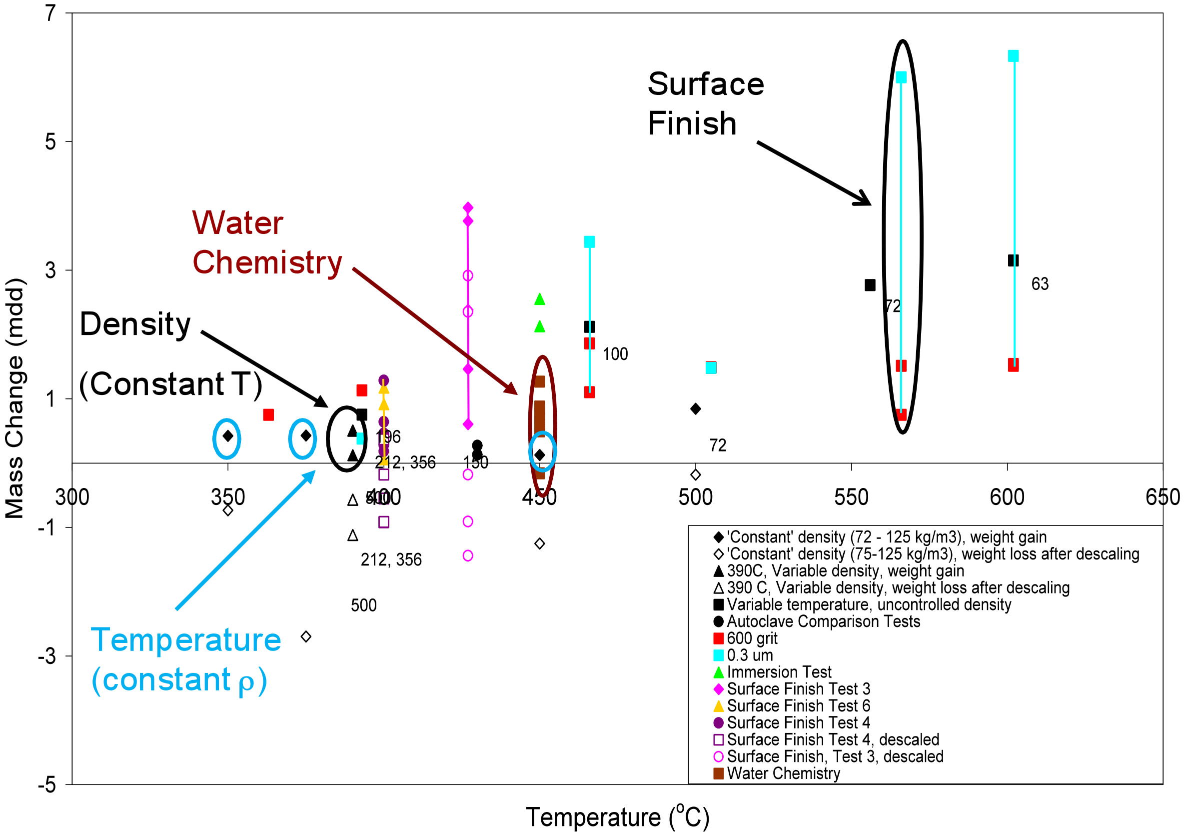

Figure 2: Mass change for 304 SS as a function of temperature for various test conditions of density, water chemistry and surface finish. Groups of data in which only one parameter was altered are indicated. Filled symbols are weight change before de-scaling, open symbols are weight change after de-scaling [10].

2.4. SCC tests

The fuel cladding material, as well as alloys for other Class I components, must be resistant to SCC. Under boiling water reactor (BWR) oxidizing hot-water conditions, sensitized austenitic stainless steels are known to suffer cracking [3]. Many factors affect the SCC susceptibility of an alloy in a given environment; some of the key factors are alloy composition and microstructure (including the degree of cold-working), chemistry of the environment (such as the content of oxygen in the water, which determines the electrochemical behaviour of a metal or an alloy), and the mechanical loading condition including the rate of loading (the so-called strain-rate). The results of a SCC data survey are shown in Table 1; SCC can occur as either intergranular cracking (IGSCC) or transgranular cracking (TGSCC) in slow-strain rate testing.

The effects of strain rate on SCC of austenitic stainless steels under BWR and PWR water chemistry conditions have been well studied. The role of bulk or crack tip plasticity is generally understood from the viewpoint of a slip-dissolution/oxidation process that governs the crack formation and growth. Because of the strain-rate effects involved, alloys that do not exhibit SCC under static loading conditions (such as in U-bend tests or even capsule tests) can be readily cracked under dynamic loading, such as in slow strain rate testing (SSRT), under identical environmental conditions.

Table 1: Mode of cracking of alloys tested in SCW conditions

Alloys	Alloy type	TGSCC	IGSCC
304	Austenitic	x	x
310	Austenitic	o	x
310+Zr	Austenitic	o	o
310+T+Nb	Austenitic	o	o
316	Austenitic	x	x
321	Austenitic	o	o
600	Austenitic		x
625	Austenitic		x
690	Austenitic	x	x
718	Austenitic		x
800H	Austenitic		o
T91	Ferritic	o	o
HT9	Ferritic		x
F82H	Ferritic	o	o
C276	Austenitic	o	o

Novotny et al [12] reported the strain rate effect in their work on 316L for a strain rate range of 1×10^{-7} s^{-1} to 6.7×10^{-7} s^{-1} with the oxygen concentration controlled at 5 200 and 900 ppb in various tests conducted at 550°C. The results revealed that the combined effect of the strain rate and oxygen concentration correlated well with the fraction of SCC area on the fracture surface: the high-strain rate/low oxygen condition produced less SCC in the sample and the low strain-rate/high oxygen condition produced the most cracking with SCC facets accounting for up to 15% of the fracture surface.

Because of a lack of suitable facilities, to date no SCC testing under controlled loading conditions has been performed in Canada. In specifying the SCC/corrosion fatigue test system recently installed at the CANMET Materials Technology Laboratory (CANMET-MTL), the likely effects of various test parameters, as discussed in the preceding sections, were considered. Details of the new SCW corrosion test facility are described in the following sections.

3. Supercritical Water Corrosion Test System: Capabilities

In early 2011 a state-of-the-art system for corrosion, slow strain rate (SSRT) and cyclic fatigue (CF) testing under SCWR conditions was installed at CANMET-MTL's Hamilton facility. The SCW corrosion test system is made up of two major parts: a water conditioning loop and a high-temperature autoclave outfitted with a mechanical loading frame. There are also two stand-alone autoclaves that can be used to pre-condition samples in preparation for testing in the main system or to perform static corrosion testing at elevated temperature and pressure.

A schematic of the SCW corrosion test system is shown in Figure 3. The overall operation of the system is as follows: water is stored at low pressure and temperature in the reservoir tank where its chemistry can be adjusted by bubbling an inert gas, hydrogen gas or oxygen gas. The chemistry of the water in the loop may be further modified by liquid additives, which are introduced via a metering pump. In order to achieve supercritical conditions in the test chamber autoclave, the water passes first through a high-pressure pump and then through a heat exchanger, which raises the temperature of the water to around 200°C. The water is then heated above the critical point as it passes through the pre-heater, on the way to the autoclave where the test specimen is loaded. Figure 4 shows the SSRT test unit as part of the overall loop.

The supercritical water exiting the autoclave is cooled to near room temperature in two stages before passing through a high-pressure filter to remove any corrosion products or debris. The pressure of the water is reduced as it passes through the loop back-pressure regulator (BPR). Finally the water passes through an ion exchange column before returning to the reservoir tank.

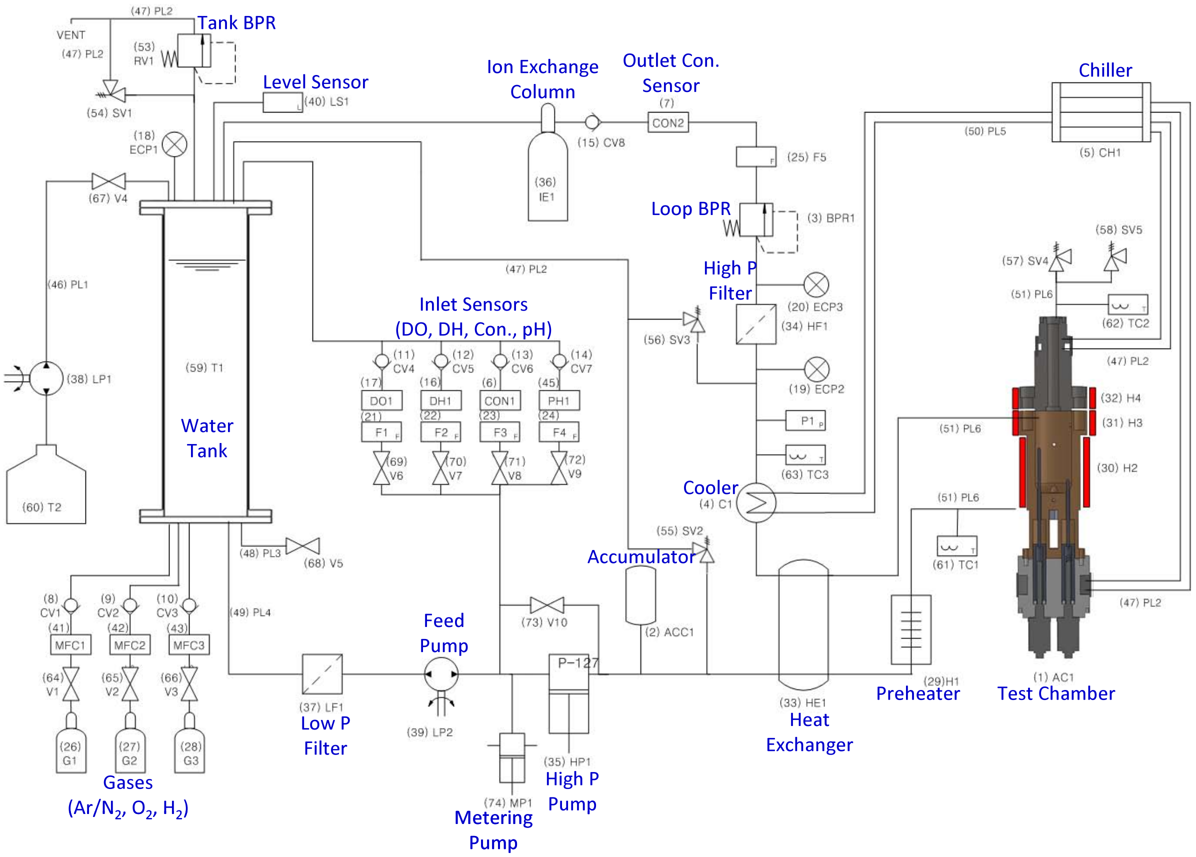

Figure 3: Schematic of the Supercritical Water Corrosion Test System at CANMET-MTL

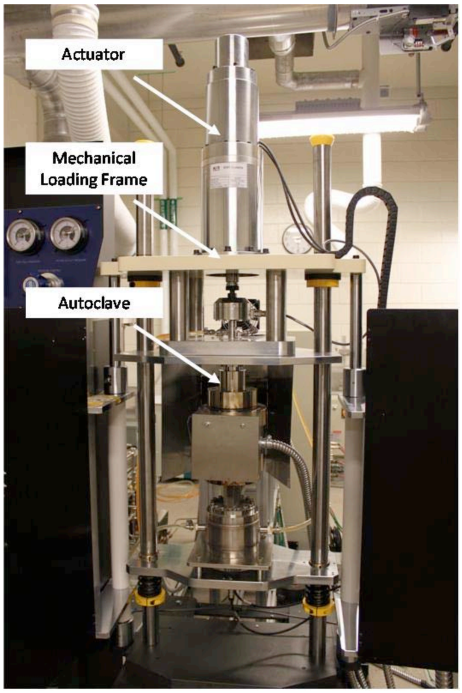

Figure 4: Photograph showing the components of the test chamber: actuator, mechanical loading frame and autoclave.

3.1 Water condition monitoring and control

3.1.1 Water chemistry

The chemistry of the water in the SCW test system is monitored real-time at two locations: dissolved oxygen (DO), dissolved hydrogen (DH), pH and conductivity are measured after the low-pressure filter, before the water is pressurized by the high pressure pump. This sample represents the water composition at the test chamber inlet. In order to probe the changes in water conductivity resulting from the corrosion of the test coupons in the high-pressure autoclave the conductivity of the water exiting the test chamber is also measured just prior to the ion exchanger. The data from the five sensors is recorded in real-time by the system control software. Aside from the inlet (DO, DH, pH, CON1) and outlet (CON2) sensors, there are three liquid sampling points: one immediately after the water tank, one at the DH sensor and one at the outlet conductivity sensor (before the ion exchange column). With proper sensor calibration the DO and DH levels can be measured with accuracies of ±0.1 ppb and ±2 ppb, respectively.

The water chemistry of the SCW loop is controlled primarily at the water tank by changing the flow rate of the inert, hydrogen and oxygen gases. DO and DH levels of <10 ppb are typical for routine testing and are maintained by the constant bubbling of argon gas through the tank water. When a DH level of 2 ppm or higher is desired, the pressure in the water tank must be increased to above 35 kPa using the tank BPR.

The chemistry of the water may be further modified by liquid additives (e.g. hydrazine) via a metering pump, should such conditions be required for a particular test program.

3.1.2 Temperature, pressure and flow

The operating parameters of the SCW corrosion test system are:

SCW Loop and Test Chamber	
Temperature	500 °C (nominal)
Pressure	27 MPa max
Flow Rate	15 L/hr max
Autoclave Volume	1 L
Water Tank	
Temperature	50°C max
Pressure	0.5 MPa max (0.1 MPa routine)
Volume	50 L

The temperature of the loop is monitored by thermocouples at the pre-heater, test chamber autoclave and following the cooler. Water temperature is controlled by the system control software, which allows the operator to specify the target temperature of the water in the pre-heater and autoclave as well as the heating rate. The autoclave band heater is used to maintain the temperature of the test chamber.

The autoclave outlet stream is cooled to near-room temperature in two stages, passing first through the heat exchanger to reduce the temperature to around 200 °C and then through a second heat exchanger (the cooler) in which the cold leg contains water at 10°C from a separate chiller. This chiller also provides cooling water to the test chamber rod seals (where the loading frame rods enter the autoclave), the temperature of which must not exceed 40^{o}C.

The pressure of the tank and loop are controlled by manually by setting the two BPRs. The pressure of the high-pressure section of the loop (between the high pressure pump and the loop BPR) is maintained by the action of the high-pressure pump. This pump is connected to an accumulator that dampens the pressure fluctuations resulting from the diaphragmatic action of the pump, providing a near-constant pressure in the high pressure section of the loop.

The loop water flow rate is monitored by a flow meter placed just after the loop BPR and controlled manually by setting the flow rate of the feed and high pressure pumps.

3.2 SCC testing capabilities

The operating parameters of the mechanical loading system are:

Tensile Load	20 kN max
Crosshead Speed	0.0001-10 mm/min
Displacement range	50 mm max
Frequency	0.001-1 Hz

The control software for the mechanical loading frame allows the operator to perform tests in SSRT or cyclic fatigue (CF) mode, under either displacement or load control. The test apparatus includes a special displacement sensor (a Balluff sensor) that directly measures the change in the sample gauge length. The control software calculates displacement values from both the Balluff sensor reading and the rotation of the actuator motor, and the operator can use either of these values to control a test or plot a curve. However, only the Balluff reading is used to calculate the strain.

During SSRT the desired load or strain can be applied using either a ramp or dwell function. The operator defines the loading or strain rate by specifying the time over which the desired change in load or displacement should occur. During CF testing the operator may choose from three control waveforms for cyclic loading: sine, triangle or trapezoid.

3.3 Stand-alone autoclaves

One 1-L and one 0.5-L stand-alone autoclave capable of operating at 35 MPa and 600^{o}C were also acquired. The autoclaves may be used to pre-condition samples prior to SSRT or CF testing in the loop system, or they may be used for static corrosion tests.

4. Other facilities available for corrosion studies

In addition to the Supercritical Water Corrosion Test System, the advanced surface and microstructural characterization facilities at CANMET-MTL can be used to explore the oxidation/passivation mechanisms occurring in SCW. This suite of equipment complements those that will be installed at the Centre for Advanced Nuclear System (CANS) at McMaster University, which will be rated for handing materials with some degree of radioactivity. The equipment installed at CANMET-MTL includes:

1) Field Emission Scanning Electron Microscope (FEI NanoSEM) with EDS, WDS and EBSD capabilities.

2) Dual Beam Focused Ion Beam Microscope (FEI NanoLab) with EDS, EBSD, and STEM detection. It has high-resolution imaging (electron and ion beam) and an Omni probe for producing lift-out TEM specimens. The system is equipped with gas injectors for precision deposition and etching.

3) Field Emission Transmission Electron Microscope (FEI Osiris) with EDS, EELS and high-angle annular dark-field imaging.

At CANS of McMaster University, the hot-cell characterization lab will be equipped with a hot dual-beam FIB, a FE-SEM, a 3D Atom Probe and a FE AES system. This advanced micro-beam centre for radioactive materials fills in another scientific infrastructure gap in Canada.

5. Conclusions

Continuing Gen IV research in Canada and within the GIF community has identified critical knowledge and data gaps in the area of SCWR materials, particularly those related to corrosion and stress corrosion properties. In order to perform SCW corrosion and SCC assessment on candidate alloys under a variety of well-controlled test conditions, an advanced SCW loop equipped with slow strain rate and corrosion fatigue frames has been installed in Hamilton. The capacity to control precisely the loading conditions in a SCC test and to control the concentrations of oxygen and hydrogen in the supercritical water will enable a wide range of studies to be performed for probing the behaviour of commercial and prototype alloys.

The installation of advanced micro-beam facilities at CANMET-MTL and McMaster-CANS will further expand Canada’s research capability in the field of nuclear materials.

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