Assessment of corrosion and stress corrosion cracking results for SCWR development: Gaps and Needs

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Abstract

International efforts on materials evaluation for the development of supercritical water-cooled reactors (SCWRs) have produced a considerable amount of corrosion test data in the open literature [1]. These data are helping guide the selection of candidate alloys for further, longer-term evaluation. As continuing research in this area advances, the gaps and limitations in the published data are being identified. These gaps can be seen in several areas, including the test environment and the severity of test condition as compared with reactor service/operating condition. While some of these gaps can be filled readily with existing capabilities, others require major investments in advanced test facilities.

1. Introduction

This paper provides a short summary of literature published on corrosion and stress corrosion cracking of metals and alloys in supercritical water, which is the coolant for the pressure vessel and pressure tube SCWR concepts. The CANDU-SCWR is a logical evolution from the current CANDU III and ACR-1000 design [2]. One of the research priorities in the area of materials is selection and/or development of alloys for use as in-core components. The performance parameters considered include general corrosion rate in high and low-density water (i.e., in the sub- and super-critical states), stress corrosion cracking (SCC) susceptibility (intergranular and transgranular), creep resistance at temperatures up to 850 °C, microstructural stability at high-temperature over the service life time of relevant in-core parts and resistance to radiation-induced damages at the dose level expected in the relevant in-core locations.

Nickel based alloys are traditionally the preferred materials for high-temperature applications. However, there are serious limitations on the use of this class of materials in in-core due to He gas production from the transmutation of Ni. Accumulation of He in the Ni alloys will eventually lead to gas bubble formation and loss of mechanical strength. There are multiple international efforts currently underway to assess various other high-alloy materials including those with high-chromium (over 18% Cr), oxide-dispersion strengthened (ODS) austenitic and ferritic stainless steels. ODS alloys are generally more difficult to weld; any melting of the parent material during conventional welding will destroy the strengthening role of nano-sized oxide, thus advanced welding techniques are needed.

As a consequence of corrosion, metal ions can be released into the coolant in the high water-density locations, where the solubility is high, then can be transported to down stream low-density sites, where they can precipitate out, causing loss of thermal transfer and crud formation [3].

In light of the expected operating conditions of the key in-core components, such as fuel cladding, and considering the type of data needed for future materials selection and eventual materials code specification, significant gaps in the area of corrosion can be identified in this literature review. These gaps can be seen in several areas, including test environment and the severity of testing as compared with reactor service/operating condition. While some of these gaps can be filled readily with existing capabilities, others require a significant investment in advanced test facilities.

2. Review of published data relating to corrosion and SCC in SCW

2.1 General comments on the published data on general corrosion

As part of the effort for developing a SCWR corrosion database, a large set of data are being collected from various sources. At the time of writing this paper, a total of 525 data sets have been collected for over 95 alloys over a range of test temperature and pressures. These data have been generated by various international researchers from as early as 1950s [4] to as recent as November 2009 [5]. The preliminary version of the SCWR corrosion database [6] is a useful tool for analysis of the collected data. Figure 1 is a distribution of the test data among five temperature ranges from 50 °C to 732 °C. As this database was designed for the SCWR applications, only limited number of results are included for tests in subcritical water. In the supercritical water regime, the majority of the data are in the temperature range of 450 °C to 538 °C.

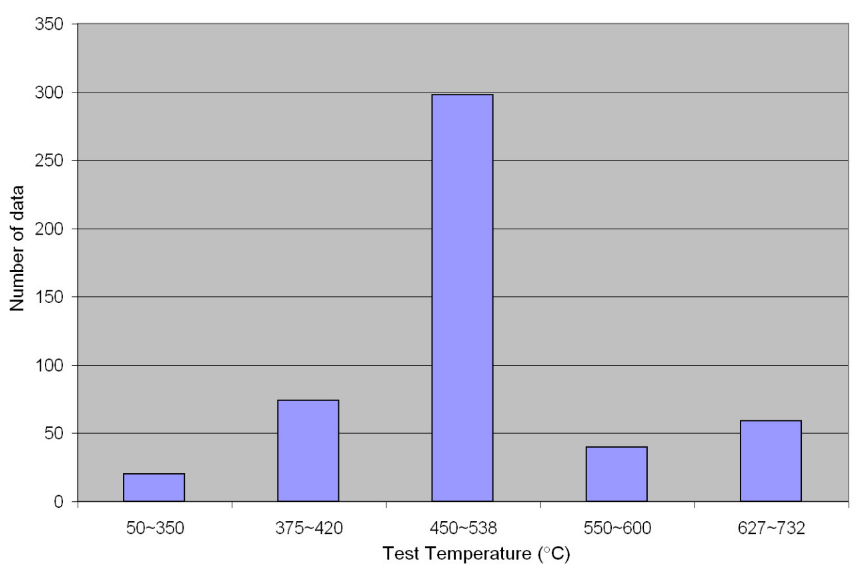

Figure 1 Distribution of the test data among five temperature ranges from 50 °C to 732 °C.

For temperature in the range of 550 to 600 °C, the number of reports is limited. Most of the data in this group were produced in the last few years, including the one by Hwang et al [7]. For temperatures above 700 °C, the only data set collected are from one research group, published in 1957 by Boyd and Pray, on corrosion and SCC of 12 Ni-Cr-Fe alloys (410, 302, 347, 309, 310, 17-4PH, 17-7PH, A-286, Inconel X, Hastelloy F, X, AMS5616) [8].

A detailed discussion of the effects of temperature and effects of key alloying elements (Cr, Ni, C, for example) has been provided in a companion paper of this proceeding, by G. Gu et al [9]; some general observations are given here.

1) Over the temperature range from 500 to 600 °C, nickel-based alloys outperform iron-based ones under similar test conditions, as shown in Figure 2. Unfortunately, because of He gas production from the transmutation of Ni, the use Ni-based alloys in thin-wall (such as cladding) or highly stressed in-core components would be limited.

For iron-based alloys, the general corrosion rate is sensitive to the content of Cr, despite the various influences of other elements such as Ni, Mo, Al, W. As the content of Cr increases, the corrosion rate decreases. T/P91, a well reported alloy with a typical 9Cr-1Mo-V-Nb composition, is often used as a baseline test material [10]. It has a corrosion rate as high as several mg/dm^2/day in de-aerated SCW at 500°C. This rate can go up by 300% at 600°C [10]. Such high corrosion rates will not be acceptable for in-core or out-core applications. In a comparative study by Was et al. [1] of NF616 (9Cr-.5Mn-.5Mo) and HCM12A (11Cr-.6Mn-.3Mo) at 500°C and 600°C, the higher Cr alloy showed a reduction in corrosion rate over NF616 at 500°C; but at 600°C the rate of weight change of HCM12A is about 30% smaller than that of NF616.

A more recent report by Kimura et al [11] showed that, when the Cr content in an ODS modified ferritic steel is increased from 14% (14Cr-1Al) to 16% (16Cr-4Al) and then to 19% (19%Cr-4Al) and finally 22% (22Cr-4Al), the weight change as a result of corrosion in 510°C SCW (25 MPa) consistently decreased from about 0.25 mg/cm^2 to about 0.07 mg/cm^2 in 1200 h tests.

2) For most alloys, the measured weight change, reported mostly as weight gain, increases with increasing temperature. This is very well anticipated given the general dependence of corrosion kinetics on temperature. What is interesting is the rate of increase in corrosion rate as the temperature is increased from 500 to 550 and then 600 °C. Betova [12] and Zhang [13] have both observed this transition in their respective work. Betova suggested the more rapid oxidation over 500 °C 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 on the alloy surface at 550 and 600 °C.

3) For the same alloy and under the same test conditions, there is a significant degree of scatter in the published data, reflecting the various procedures of sample preparation used by various workers, variation in alloy composition within the specified range and difference in the microstructure of samples used.

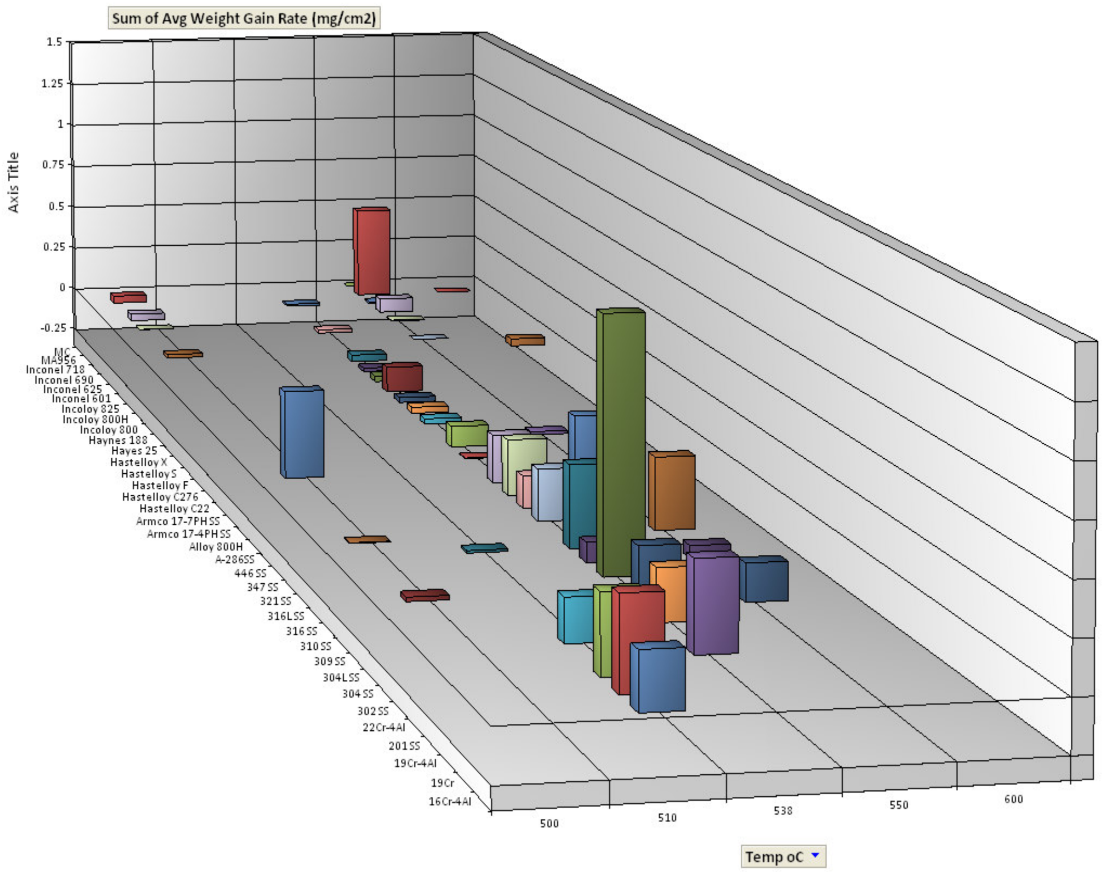

Figure 2. Variation of corrosion rate as a function of temperature using the data collected in the MTL-AECL Corrosion database [6, 9] (only alloys with Cr content greater than 16% are plotted)

2.2 Comments on SCC data

The fuel cladding material, as well as alloys for other components, must also be resistant to SCC in the SCW coolant. Therefore, the SCC properties of candidate alloys, under un-irradiated and irradiated conditions, are of great importance for the SCWR development. The SCC susceptibility of a number of common alloys has been evaluated by various workers under SCW conditions. As of mid-February 2010, 33 papers have been collected on the subjects. Table 1 lists the test conditions for these SCC tests. Most of the SCC reports in the past decade have been generated by Was' Group [1,10], as part of their research output of a prior SCWR national program on SCWR development in the USA.

Table 1. Summary of SCC tests surveyed in the open literature

Paper Number	Alloy	Temp. (c)	Pressure (MPa)	[oxygen,ppb]	[hydrogen]	Test method	Test duration (hr)
SCC-001	F/M steels, austenitic SS, Ni,Zr,Ti-base alloys	from 400 to 732	25	<10ppb-8ppm		CERT	100-1000
SCC-002	F/M steels, austenitic SS, Ni,Zr,Ti-base alloys	from 250 to 732	25-60	<10ppb-8ppm		CERT	100-1200
SCC-003	316L,316LGBE,690,690GBE	500	24	<10ppb		tensile	
SCC-004	T91, HCM12A, HT-9, weld T91, weld HCM12A	400-600	25	100, 300 appb		tensile bar	
SCC-005	316L, D9, 690 and 800H	400-500	24	<10ppb		CERT	
SCC-006	316L, 690	500	24	<10ppb		CERT	
SCC-007	304, 316, 690	<600	<30	<10ppb		CERT	
SCC-008	304, 316, 690	385-550	23.4-27.6			CERT, CGR	
SCC-009	316	288-500	from 10 to 25	<10ppb-2ppm			32-470
SCC-010	304,316,625,690	400-550	25.5	<10ppb			184-608
SCC-011	A718, A690	400, 600	25			CERT	
SCC-012	304,316,600	290-550	25	8ppm		SSRT	
SCC-013	304,316,625,690	500, 550	25.5	<10ppb, 8ppm		CERT	
SCC-014	625, 718	500, 600	25	<10ppb, 2ppm			1026
SCC-015	Review paper						
SCC-016	625	<500	<37				150
SCC-017	316	400	25, 60	8, 800ppm		SSRT	
SCC-018	316,625,C-276,MC-alloys	400	25	8ppm		SSRT	
SCC-019	800H, HT-9	370-600	25	2ppm		tensile bar	1026
SCC-020	Ni-based and Fe-based alloys	400-500	22-25			SSRT, CL	
SCC-021	316L, 690	400-500	25	<10ppb		CERT	
SCC-022	Review paper						
SCC-023	T91, T92, T122, 625, 690, 800H, MA956	370-600	25	<10ppb		U-bend sample	200
SCC-024	316, 625, HC276, MC alloy, MAT21	400	25		up to 8 Mpa	SSRT	50
SCC-023	316, 304						
SCC-026	F82H	290-550	23.5	0.2ppm		SSRT	1000
SCC-027	12 SS and Ni-base alloys	up to 732	34.5	degassed water		capsule	3168
SCC-028	304 ss and 718	600	25			capsule	

The general observation is that 3XX series stainless steels such as 304 and 316 are prone to SCC, as well as many Ni-based alloys such as Alloy 600, 625, 690 and 718. On the other hand, ferritic materials such as T/P91 and F82H showed good immunity to SCC in the tests reported to date. SCC in metals and alloys can take a path along or at the grain boundary (IGSCC) or transverse the grain structure (TGSCC). Table 2 summarizes the mode of cracking in these alloys that ware found to be susceptible to SCC.

Table 2. Mode of cracking of alloys tested in SCW conditions

Alloys	TGSCC	IGSCC
304	x	x
316	x	x
600		X
625		x
690	x	x
718		x
T91	O	O
HT9		x
F82H	O	O
C276	O	O
MC	O	O

It should be pointed out most SCC tests have been conducted using the slow-strain rate technique (SSRT), alternatively known as constant extension rate tests (CERT). Tests using pressurized capsules, as well as tests using U-bend samples, have also been reported by a few groups [7,8,14]. Different test technique can sometime produce very different results of the susceptibility of an alloy. For example, in a study in supercritical water containing hydrogen peroxide (up to w.t.10%.), Alloy 625 was shown to be sensitive to SCC in slow strain rate tension both at 400° and 500°C under a pressure of 25 MPa [14], whereas constant load tests did not show any significant amount of cracking when the applied constant stress was at 100% and 140% of the yield strength. This shows the role played by the dynamic plasticity at the metal surface in the SCC initiation and propagation process, a phenomenon well known for SCC in subcritical water and in other metal-environment SCC systems.

In a SSRT or CERT test, test samples are strained to failure and then the presence or absence of stress corrosion cracks is confirmed by post-mortem examination. The technique is very severe in comparison with real-life stressing conditions, as the cracks are usually developed after the yield point of the alloy has been exceeded, and, in fact, they could have initiated any where between the yield and the UTS point of the alloy on its stress-strain curve. SCC or CERT tests are commonly carried out for materials susceptibility study. However, in terms of data generation for alloy qualification or confirmation of code requirement, these tests have little value, as discussed in the following section.

One of the most interesting results is the effect of water pressure on the SCC mode, as shown in Figure 3. Watanabe et al [15] performed this SSRT test on 316 ss in SCW temperature of 400 °C and a strain rate of $2.78*10^{-6}$/s. The 316 alloy exhibited intergranular cracking at high pressure (P>35 MPa) but the cracking changed to an transgranular mode at lower water density (pressure at 25MPa and 30 MPa). This result highlights the complexity of the SCC process in general; for SCC in SCW, in particular, the mechanism of cracking remains largely unexplored.

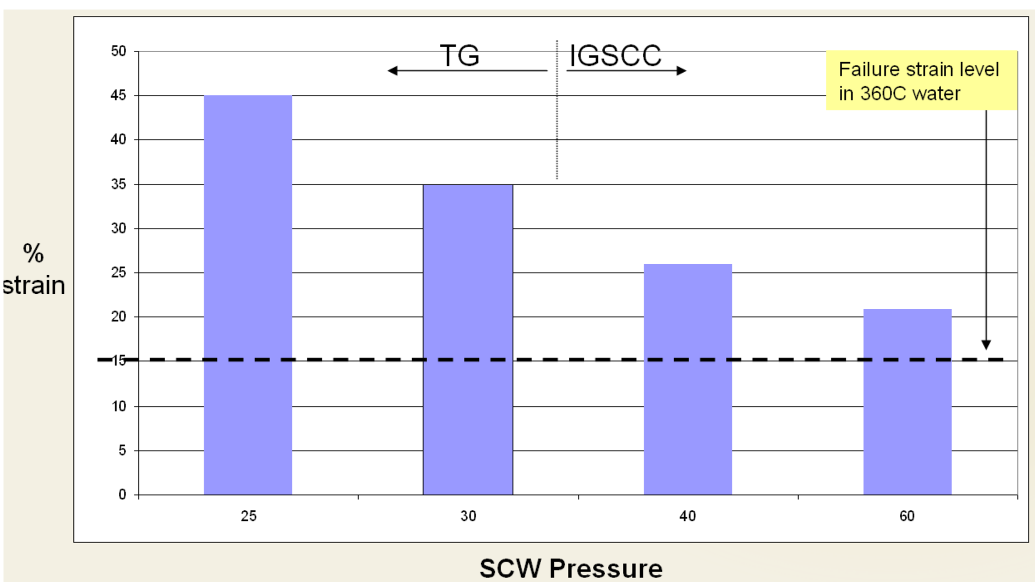

Figure 3. Variation in SCC susceptibility and change in failure mode as a function of water pressure for 316 tested at 400 °C and a strain rate=$2.78*10^{-6}$ s-1 (Graph generated using data in [15])

3. Gaps and needs

Although materials R&D for SCWR development has been going on, in a rather intermittent fashion for many decades, dating back to the 1950s [4], many gaps exist in key areas of alloy selection and development. In terms of the CANDU-SCWR design in which the cladding surface temperature can reach as high as 850 C [2], critical mechanical and corrosion data are yet to be produced even for un-irradiate materials.

The issues with mechanical performances of commercial alloys for SCWR development are discussed in another paper of this proceeding [16], this paper addresses aspects related to corrosion resistance of materials and water chemistry.

3.1 Research gaps and needs related to the chemistry of the test environment

The chemistry of the test environment is an area where significant gaps exist. Most of the data produced so far are for pure water in the supercritical state; the effects of various coolant additives, which are likely necessary in order to control the radiolysis of the direct-cycle feed water, are largely unknown [17]. Co-ordination of materials and chemistry research with both the in-core and out-of-core design parameters in mind is critical. Identification of the important parameters (e.g., corrosion rate, radiation resistance, mechanical properties) essential for each component requires knowledge of the expected environment (temperature, pressure, water chemistry) that these components will be exposed to, and like-wise, the development of key chemistry specifications (e.g., feedwater metal concentrations at the core inlet, agents for radiolysis control, etc.) relies on the data of metal release rate for candidate alloys in both sub- and supercritical water.

3.2 High-temperature SCW tests

As the surface temperature of the fuel cladding in a CANDU-SCWR can reach as high as 850 °C, corrosion and stress corrosion data are required for this high temperature range. Corrosion tests at high temperatures can be difficult to do, particularly for temperatures higher than 650°C, as there is, if any, a very limited supply source of relevant test equipment. The highest temperature corrosion testing in SCW known to date was 732°C, in work carried out at Battelle in the mid-1950s using static pressure-capsules [8]. In this work, cracks were found to develop in 316 and 310 SS; deep pits were observed in 347 SS. In the alloys with notable amounts of carbon, decarburization up to 100 microns deep into the alloys was found after 132 days testing; all test materials showed carbide precipitation, which can lead to localized corrosion and nodule formation on the surface [8]. A fundamental challenge is that, with the increase in temperature, an increasing number of precipitates would start to form slowly in the microstructure, which could have strong effects on long term SCC or even general corrosion properties. This aspect of the metallurgical effects is yet to be studied.

3.3 Gaps in SCC and corrosion fatigue data

Reactor and power plants materials are subject to various national and international codes and specifications. For pressure-containing components such as feeder pipings and header sections in the case of a CANDU-SCWR, which will be the so-called Class I components in the ASME codes, the governing design rules for a particular part consist of 1) load-controlled stress limits (primary factor) (for details, see ASME Section III, Div I-NH Appendix I) and 2) strain, deformation, and fatigue limits (see Section III, Div I-NH Appendix T).

While the load-controlled stress limits are based on time-dependent allowable stresses from both tensile test results and long-term creep tests, the second group of design rules i.e., strain, deformation, and fatigue limits, require significantly more effort to satisfy. These latter rules deal with complex materials-stress-environment behaviour involving deformation, corrosion, creep-fatigue damage, corrosion-fatigue and stress corrosion cracking.

To illustrate this point, Figure 4 demonstrates how the effects of subcritical water at 300 °C and at ambient pressure are integrated into the fatigue limit design in the most recent ASME Section III codes.

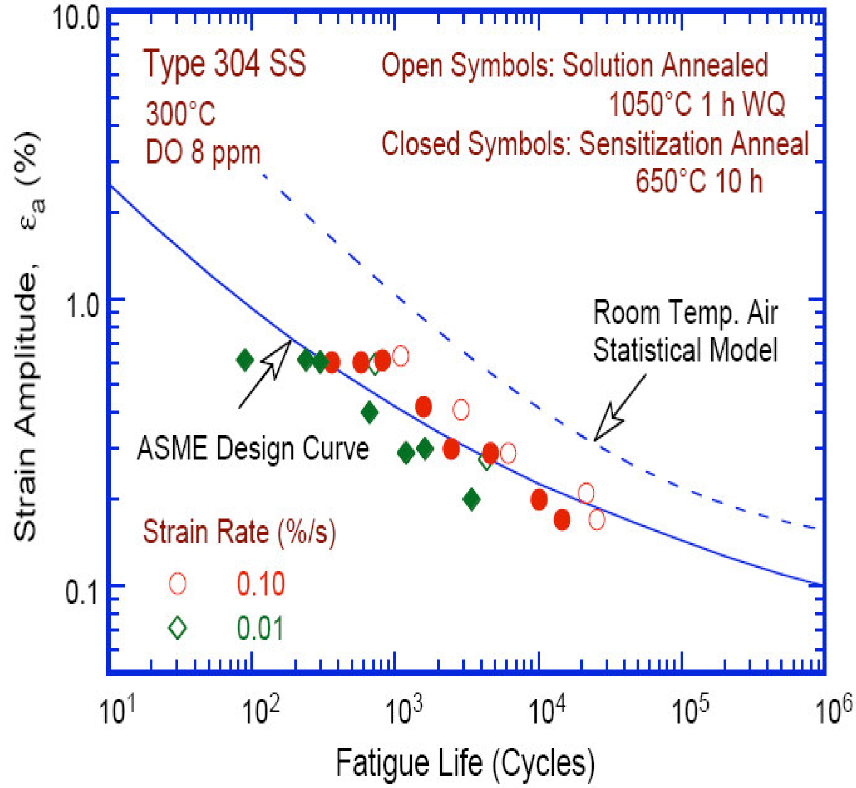

Figure 4. ASME design curve for 304 ss used in subcritical water (Courtesy of ANL)

In the 1970s when reactor materials were selected, the design data were based on the fatigue test results for ambient atmospheric environment. The subsequent design specification used a factor of 2 on stress and 20 on load cycles, whichever is largest, of the room-temperature data, which is represented by the solid blue line in Figure 4.

However, when the same alloys are tested in water at 300 °C, many of the fatigue data fall below the safe design zone (the blue line) and this effect of water is more drastic as the strain rate in the loading cycles is lowered; the latter being a typical corrosion fatigue characteristic.

Corrosion fatigue data for alloys in SCW water are very limited. In a reported case of corrosion fatigue [18], corrosion fatigue crack growth rate in P91 alloys was found to be twice as fast in SCW of 500 °C and 25 MPa as compared with subcritical water at 370 °C. A loading frequency of 10 Hz was used in this work, which is too fast to be relevant to many reactor Class I components. Tests at slower loading rates, for example, in a strain rate range of 0.01 to 0.001/s, would take much longer time.

3.4 Gaps inadvanced alloys.

Alloys that are resistant to creep, corrosion and irradiation, to name a few key materials parameters, are needed for the development of SCWRs. Recent research on supercritical and ultra-supercritical fossil power plants has made many advances in the area of materials [19, 20]. The materials researchers for the fusion reactor (e.g., the ITER program) have also made important progress in developing irradiation-resistant alloys, including the development of advanced ODS alloys. Similar effort on alloy development for SCWR is just starting.

It is interesting that while these different energy-production systems operate under very different physical and environmental conditions, the underlying fundamental principles guiding materials development are often shared amongst these applications. There is therefore an opportunity to gain a significant amount of mutual support by building a synergy amongst these various materials groups. Unfortunately there is no coordinated formal mechanism for the workers in these different research areas to communicate.

4. Concluding remarks

The ongoing corrosion-related research in the Canadian SCWR program aims to advance our knowledge of materials in this area with potential application in a pressure tube SCWR. There remain many 'knowledge' gaps regarding corrosion properties, including the chemistry of the test medium, test conditions and test methods used.

The experimental challenges as well as gaps in advanced test facilities for future development are also becoming evident. New facilities and equipment are being set up in Canada to meet various identified needs, including processing facilities for ODS materials, corrosion test facilities (engineering and bench-scale SCW loops and autoclaves), corrosion fatigue testing system, high temperature creep and creep-fatigue testers 9up to 1100 °C), specialized transmission electron and focused ion-beam microscopes for handling radioactive samples. As a member of GIF, Canada will continue to expand its own internal materials research capabilities and will work collaboratively with its GIF international partners to address these gaps in order to support the international development of an SCWR system.

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