CHALLENGES IN MECHANICAL PERFORMANCE OF MATERIALS IN SCWR

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Abstract

The Super Critical Water-cooled Reactor (SCWR) system is a high temperature, high pressure water-cooled reactor that operates above the thermodynamic critical point of water. This aggressive environment, together with irradiation, decreases the mechanical stability of the construction materials. Although materials for light water reactors have been used for many decades, the performance of these same materials in an SCWR is uncertain. Creep, fatigue, creep-fatigue, and fracture toughness are the main mechanical characteristics of materials that can be degraded in the SCWR environment. In this paper, the challenges involved in predicting the mechanical performance of materials in the SCWR environment, together with selecting potential materials for use in an SCWR, is discussed.

Keywords: SCWR, Candidate Materials, Mechanical Properties, Irradiation Effects.

1. Introduction

Nuclear technology is the major source of carbon-free energy. The growing demand for energy, as well as concerns about environment, has encouraged governments to collaborate toward developing more efficient and manageable nuclear technologies which are not only more cost-effective and reliable, but also proliferation-resistant. This advanced generation of nuclear reactors is known as Generation IV [1]. One of the targets for Generation IV nuclear reactors is to increase thermal efficiency by increasing the reactor operating temperature.

Generation IV International Forum (GIF) considers six reactor concepts including a new generation of water-cooled reactors, the so-called Super Critical Water-cooled Reactor (SCWR). The various proposed SCWR concepts are for high-temperature, high-pressure water-cooled reactors that operates above the thermodynamic critical point of water, i.e. 374°C and 22.1 MPa. In a reference design for generating 1700 MWe electricity, the reactor operates at a pressure of 25 MPa and a reactor outlet temperature of 510°C, possibly up to 550°C [2]. This was the reference design of SCWR in the United States and is of interest in Japan and Europe. The Generation IV SCWR concepts are primarily developed for efficient electricity production and utilize a direct power generation cycle; there are no steam generators. Instead, the Super Critical Water (SCW) from the core drives the turbine directly.

The successful implementation of an SCWR system depends on overcoming many critical barriers including the development of suitable materials and relevant technologies. Although materials for current generation water-cooled reactors have been proven for many years, the performance of these same materials in an SCWR is uncertain. The higher temperature and higher irradiation envisioned for the SCWR imply that new materials may need to be developed for such an aggressive environment. Zirconium alloys (Zircalloy-2 and -4, and Zr-2.5Nb) have been used routinely as fuel cladding and other reactor internals in both light and heavy water reactors because of their low neutron capture cross-section and acceptable mechanical and corrosion resistance at high temperatures, up to 380°C under normal service conditions, in an aqueous environment. Although some high-performance zirconium alloys

may still qualify, the SCWR conditions would limit the use of zirconium alloys because of increased susceptibility to hydrogen embrittlement due to severe hydride formation, allotropic phase changes at higher temperatures (α to β phase), poor creep properties and significant oxidation at high temperatures [3-5].

Materials research for the SCWR in the Canadian National Generation IV program focuses on corrosion and stress corrosion cracking, radiolysis and water chemistry, dimensional and microstructural stability and strength, and embrittlement and creep resistance of fuel cladding and structural materials. In the present study, anticipated challenges in the area of mechanical properties of materials in the SCWR environment are highlighted.

2. SCWR plant

There are currently two general concepts envisioned for the SCWR. In the pressure vessel concept, the entire reactor core is contained within a large pressure boundary, the reactor pressure vessel (RPV). In this concept, the coolant, at pressure and temperature of 25 MPa and 280°C, enters the RPV and is heated to about 500°C and delivered to the power conversion system (turbine), which is similar to that used in super-critical fossil-fuel-fired plants. In one study, the anticipated dimensions of such an RPV for SCWR is 12.40 m high, 5.32 m inside diameter, and 0.46 m wall thickness (note that the RPV wall thickness depends on the material used in its construction) [6]. The other design is based on the CANDU¹ reactor concept, and utilizes individual pressure tubes rather than a single large pressure vessel. In current designs, the coolant pressure is contained in much smaller tubes, about 10 cm in diameter, which contain the fuel bundles. A large low-pressure tank known as calandria vessel contains all the pressure tubes passing through the calandria tubes. Figure 1 demonstrates the arrangement of a fuel bundle, pressure tube, and calandria tube.



Figure 1. Illustration of the current CANDU pressure tube technology [7].

Conceptual designs of the CANDU-SCWR, similar to the current CANDU design, use a heavy water moderator with the fuel bundles located inside pressure tubes [8], but use an insulated fuel channel to eliminate the need for calandria tubes. The coolant that runs inside the pressure tube and through the fuel bundles would be light water at a pressure of 25 MPa and a core inlet temperature of 350°C and a core outlet temperature of up to 625°C.

The results of most material research for either the pressure vessel design or the pressure tube design would benefit both, especially for the materials to be used in the out-of-core sections.

¹ CANDU[®]: <u>CAN</u>ada <u>D</u>euterium <u>U</u>ranium is a registered trademark of Atomic Energy of Canada Limited (AECL).

Therefore, the potential challenges in mechanical performances of candidate materials related to both designs are addressed here.

3. **RPV-type SCWR**

In the reference design proposed by the United States [9], the SCWR RPV is exposed to temperature and pressure of 500°C and 25 MPa as well as irradiation. Therefore, materials with high thermal conductivity and low thermal expansion coefficient would be prime candidates for construction as they are less susceptible to thermal fatigue. Moreover, the candidate materials are required to be resistant to damage associated with neutron irradiation, e.g. swelling. Because of these considerations, ferritic and ferritic/martensitic (F/M) steels are preferred over stainless steels [10]. Over the past few decades, F/M 9-12%Cr-Mo steels (all chemical compositions are in weight percent throughout this paper) have been developed for applications at high temperatures and successfully used in the fossil-fuel-fired plants and chemical industries. This class of heat-resistant steels exhibits high creep rupture strengths at temperatures as high as 600°C [10]. Nevertheless, their mechanical performance under irradiation is not well understood as they were principally developed for non-nuclear applications. Thus, the use of these materials in an RPV would require significantly more development and qualification. Corrosion characteristics must also be taken into account when comparing different chemistries. Both 9%Cr and 12%Cr F/M steels exhibit double layer oxidation in SCW, with the latter apparently being less resistant when the SCW oxygen content increases [11]. In comparison, austenitic steels exhibit thinner oxide layers with an increase in porosity at higher temperatures [11, 12].

3.1 Creep properties of F/M steels

Grade 91 steel, with nominal composition of Fe-9Cr-1Mo-V, is a F/M steel and the reference material for the RPV shell, nozzles, heads, and several piping components. The chemistry of Grade 91 is specially designed to support the formation of a microstructure which provides excellent long-term high-temperature strength, creep and stress rupture properties. However, the high-chromium F/M steels are microstructurally unstable; mechanical properties deteriorate as the microstructure evolves and approaches its equilibrium state at high temperature over time. Therefore, effort has been made toward stabilizing the microstructure and delaying the mechanical degradation at high temperature by developing newer generations of Grade 91, i.e. Grade 92 and Grade 911 which are tungsten-modified steels. Figure 2 compares the creep rate in these three grades of chromium steel at 600 and 650°C. In the high stress region, the difference in the secondary creep rates is relatively small, whereas it becomes more pronounced in the low stress region with Grade 92 exhibiting the highest resistance to creep deformation. This indicates a change in the operating creep mechanisms. At the moment, the question is whether such a difference in creep strength will remain over the lifetime of SCWR during which the underlying strengthening mechanisms, i.e. dislocations, precipitates, and solid solution, evolve and affect high-temperature mechanical properties. This depends on the kinetics of the precipitation processes and development of metastable, and eventually stable, microstructures. On the other hand, the creep-rupture curves in this class of steels appear sigmoidal; there is an intermediate stage in the stressrupture time curve during which creep strength decreases at a faster rate before slowing down again. Consequently, extrapolating data to approximate structural lifetimes may not be a reliable approach. This calls urgently for data from long-time (>100,000 hours) creep experiments (the estimated plant lifetime is 60 years or 525,600 hours). There are some

ongoing creep-rupture tests at 600 and 650°C on Grade 91 that have already passed more than 11 years, e.g. [14].



Figure 2. Secondary creep rates for P91, P92 (P denotes piping), and E911 (Grade 911) [13].

3.2 Creep-fatigue properties

Creep-fatigue is a failure mode of great concern for reactors operating at elevated temperatures, and is one of the major issues in Grade 91. Creep-fatigue results on Grade 91 indicate that the number of cycles to failure decreases with the introduction of hold time, and the effect is more severe in an oxidizing environment [15-17]. Figure 3 compares the creep-fatigue behavior of Grade 91 (i.e. 9Cr-1Mo-V) with three other materials used in the nuclear industry. As can be seen, the creep-fatigue interaction is more severe in Grade 91 than 2.25Cr-1Mo steel that is extensively used in the fossil power plants and petroleum industries.



Figure 3. Creep-fatigue interaction for some high-temperature alloys [18].

3.3 Effect of irradiation

Non-equilibrium segregation stimulated by the vacancies and interstitials generated by irradiation can change the microstructure by formation of new precipitates that are not present in the absence of irradiation. The SCWR RPV is estimated to sustain irradiation to a peak fast fluence of $<5 \times 10^{19}$ n/cm² (E>1 MeV) [9]. Precipitates formed in the 9-12%Cr steels during

irradiation include α' , G-phase, M₆C, and Chi-phase [19-21]. This, in turn, would affect the mechanical properties at elevated temperatures. Figure 4 demonstrates the effect of irradiation temperature on yield stress and ultimate tensile strength in Grade 91. Generally, the 7-12%Cr F/M steels exhibit a hardening characteristic at irradiation temperatures up to 425-450°C caused by the high density of dislocations and dislocation tangles as well as irradiation-induced changes in precipitates [19, 22-24]. Above 425-450°C, properties are not affected by irradiation; however, there may be some enhanced softening depending on fluence [25, 26]. The softening at these temperatures proceeds through dislocation recovery and precipitate coarsening, both of which are assisted by diffusion which is enhanced by irradiation.



Figure 4. Yield stress and ultimate tensile strength of normalized-and-tempered, thermally aged, and irradiated (up to 9 dpa) modified 9Cr-1Mo (Grade 91) steel [22].

Toughness is also affected by irradiation-induced hardening, which is of great concern for nuclear applications of F/M steels and for pressure vessels for light-water reactors. Such effect of irradiation is manifested as an increase in ductile-brittle transition temperature (DBTT) and a decrease in upper shelf energy (USE), as shown in Figure 5 for Grade 91 irradiated in the High Flux Isotope Reactor (HFIR). Such damage is observed in all



Figure 5. Charpy impact properties of 9Cr-1MoVNb steel (Grade 91) in the unirradiated condition and after irradiation to 20-34 dpa at 300°C and to 37-42 dpa at 400°C in HFIR (High Flux Isotope Reactor) [27].

conventional and reduced-activation 7-12%Cr steels. However, the severity of the effect depends on both chemistry and manufacturing and heat treatment processes. The reduced-activation 9Cr-2WVTa steel shows much less shift in DBTT than the 12Cr-1MoWV steel, about 10°C vs. 125°C respectively. The Grade 91 steel has a DBTT shift about half as large as 12Cr-1MoWV for similar test conditions, which is still more than twice that for the 9Cr-2WVTa steel [27]. It should be noted that irradiation embrittlement in low alloy steels, such as A533B currently used for RPV in light-water reactors, occurs at irradiation <<1 dpa [10]. These low doses of irradiation have little effect on high alloy steels such as those discussed above [10].

3.4 General considerations

The reduced-activation low alloy 3Cr-3WV (Fe-3.0Cr-3.0W-0.25V-0.10C) and 3Cr-3WVTa steels, developed in the United States Fusion Program [28, 29], would be better candidates than A533B and 2.25Cr-1Mo steels for pressure vessels, piping, and other pressure boundary components of Generation IV reactors. Both steels have strength more than double the 345 MPa (50 ksi) used in design with the A533B steel and have advantageous creep properties over T23, T24, and T91 (T indicates tube) steels at 600°C [10].

In a different design scenario for RPV, it is proposed that the SCWR RPV be insulated from the outlet coolant temperature of 500°C and operate at the inlet coolant temperature of 280°C [9]. The inner surface of the vessel, exposed to water at 280°C, could be clad with a weld overlay of Type 308 stainless steel. Therefore, service conditions of the RPV will not be very different than those of the current generation of pressurized water reactors (PWRs). Consequently, SA 508 Grade 3 Class 1 forging or SA 533 Grade B Class 1 plate, currently used in PWRs, could be the primary candidate materials for the RPV shell. Both of these steels have similar chemical compositions, i.e., maximum 0.25% Cr and 0.45-0.6% Mo, and design stress intensities in the ASME Code. The maximum temperature allowed by ASME for SA 508 is 371°C. However, the SA 508 Grade 3 Class 1 forging is preferred to eliminate the need for axial welding.

In either case, using higher strength materials results in a significant decrease of the RPV wall thickness and provides a number of advantages such as casting smaller ingots and easier heat treatment and inspection. In this respect, the 3Cr-3WV steel discussed above could be an alternative. Present A533 grade B Class 1 and A508 Grade 2/3 Class 1 light water reactor vessels are clad with stainless steel to prevent corrosion products from contaminating the coolant. The higher chromium means that the steel is also more resistant to hydrogen embrittlement [9]. Based on observations on various higher-alloyed ferritic steels (e.g., 2 1/4Cr-1Mo, Grade 91, Sandvik HT9) irradiated to high doses (tens of dpa as opposed to <1 dpa in a light water reactor) in fast breeder reactors and fusion reactor test programs, the 3Cr-3WV steel seems highly resistant to irradiation embrittlement compared to the current light water reactor steels [9]. Another potential material being studied is the new version of A508, the so-called A508 Grade 4N Class 1 steel [30, 31]. The A508 Grade 4N Class 1 forging containing up to 3.7% Ni, higher than that in A508 Grade 3, is a generally bainitic (typically lower bainite) steel with a minimum specified yield strength of 585 MPa (85 ksi) compared with 344 MPa (50 ksi) for the A508 Grade 3 Class 1 forging. Thus, the design stress intensities would likely be about 70% higher for this alloy. Although it contains about 3.5% nickel, irradiation results at temperatures near the SCWR operating temperature of 280°C indicate it could be suitable from the standpoint of irradiation resistance. The A508 Grade 4N steel typically has a 41-J Charpy temperature below -100°C and this could be lowered to

below -150°C with an upper-shelf energy greater than 275 J (200 ft-lb) by enhanced control of tramp elements such as phosphorus, sulfur, arsenic, and antimony, as well as manganese and silicon [9, 32].

4. CANDU-SCWR pressure tube

Two major designs have been proposed by AECL for the CANDU-SCWR fuel channels: the high efficiency channel and the re-entrant channel [8].

<u>High Efficiency Channel (HEC)</u>: The calandria tube, Figure 1, is eliminated in this design and the pressure tube is in direct contact with the heavy water moderator at 80°C, Figure 6. The thermal insulator protects the pressure tube from the hot coolant at 625°C. The insulator itself is protected by a perforated metallic liner against possible damage by the fuel bundles and erosion by the coolant flow. The coolant pressure is transmitted to the pressure tube through the perforated liner and small openings in the insulator. This may also put the inner surface of the pressure tube at temperatures higher than 80°C. The amount of thermal energy transferred to the pressure tube depends on the insulator thickness, which must be determined by experiment.



Figure 6. Schematic illustration of one CANDU-SCWR fuel design; the high efficiency channel [8].

In addition to resistance to irradiation deformation, all materials for use in fuel channels should be as neutron-transparent as possible. Therefore, Zr alloys, with high neutron economy, are the prime candidates for the pressure tube. Even though the pressure tube is exposed to a lower temperature than that in current CANDU designs (310°C), the pressure and fluence are higher. As a result, the Zr alloy Excel (Zr-3.2%Sn-0.8%Nb-0.8%Mo-1130 ppm O) instead of the current CANDU pressure tube material, i.e. Zr-2.5Nb, is now being considered [8]. The irradiation deformation of annealed Excel occurs at much lower rates than cold-worked Zr-2.5Nb, and its creep rate is about 30% of that in cold-worked Zr-2.5Nb [8]. However, more data on the effect of irradiation on strength, creep, and fracture toughness are still required.

On the other hand, the insulator must have high thermal and corrosion resistance in SCW, not to mention sufficient strength to hold the weight of the fuel bundles without excessive thickness reduction during its service period. Porous Yttria Stabilized Zirconium (YSZ) is being studied as a potential material for the insulator, because it has low neutron cross-section, low thermal conductivity, and very high corrosion resistance in SCW [8, 33]. There

are also some indications that irradiation-induced embrittlement is not significant in YSZ and there is no amorphization under neutron flux [34].

The perforated metal liner must be resistant to corrosion in SCW and must protect the insulator. It must also be hard for the fuel bundles to easily slide and rest on it. Additionally, it must be resistant to wear and fretting as well as irradiation swelling. The Grade 91 steel, Incoloy 800, and low swelling stainless steels could be candidate materials for the liner tube; however, they must exhibit adequate resistance to corrosion in SCW [8, 35]. Since the liner will operate at temperatures close to the highest range for steel, i.e., 625°C, and be exposed to high neutron irradiation, the candidate materials should be evaluated for creep and fracture toughness. Depending on the process and frequency of refuelling, fatigue and creep-fatigue might be issues as well.

<u>Re-Entrant Channel (REC)</u>: This design incorporates a calandria tube, Figure 7; the pressure tube is separated from the heavy water moderator by a gas annulus, similar to the current CANDU reactors. SCW coolant enters the channel between the pressure tube and an inner tube. Then, it turns around and flows through the inner tube where the fuel resides. With this design, the pressure tube is kept at a temperature of about 350° C to 400° C [8]. In terms of strength, Zr alloys, especially Excel with UTS of about 450 MPa at 400°C, could be a possible candidate material for the REC pressure tube. Nevertheless, corrosion characteristics and irradiation deformation need to be studied as there is very limited data on these in the temperature range of interest. Chromium plating may be effective in reducing oxidation and hydrogen ingress in the temperature range of 350° C to 400° C [8].



Figure 7. Schematic illustration of alternative CANDU-SCWR fuel design; the re-entrant channel [8].

The inner tube faces similar challenges to those of the liner tube in the HEC design. However, despite the liner tube, the outer and inner surfaces of the inner tube are exposed to considerably different temperatures, i.e., 350°C versus 625°C, respectively. Such thermal gradient through the thickness, and associated thermal stresses, could bring about a more severe condition for the inner tube than the liner tube and enhance the effect of irradiation. Therefore, using materials with higher strength could be advantageous as the thermal gradient is alleviated by using thinner sections. This would also improve neutron economy.

5. Fuel cladding

The main challenge regarding the cladding of most Generation IV systems is to develop and qualify new high-temperature steels with very good swelling and corrosion resistance that maintain good mechanical properties even after high irradiation damage. Current-generation water-cooled reactors use cladding made of zirconium alloys. It is anticipated that the fuel

cladding temperature in the CANDU-SCWR could be as high as 850°C [8]. In this thermal regime, zirconium alloys cannot be used as they will lose their strength and be very susceptible to oxidation. Moreover, the high temperature irradiation-induced changes to the cladding due to swelling, helium-bubble formation, dislocation rearrangement, precipitate morphology and irradiation-induced composition changes must be taken into account to ensure that the integrity of the components for the design life of the cladding is not compromised. Transparency to neutrons is also a limiting factor in material selection for cladding. If neutron economy can be relaxed by uranium enrichment, stainless steel might be a candidate for fuel cladding material [8]. Generally, F/M steels are the reference candidate materials for cladding because of their high resistance to irradiation-induced swelling, but they are limited by high-temperature strength and resistance to creep. Also, their corrosion behavior in SCW is not well understood. The GIF community is currently examining the corrosion characteristics of this class of high-temperature steels.

Oxide-dispersion-strengthened (ODS) F/M steels are also potential candidates for cladding because they can provide the required low swelling rate and high strength at high temperatures [36]. Other proposed potential materials are Fe-35Ni-25Cr-0.3Ti, Incoloy 800, Inconel 690, Inconel 625, and Inconel 718 [37]. Austenitic (Fe-Ni-Cr) and nickel-base alloys are more corrosion resistant in SCW than ferritic and F/M steels, which have lower chromium contents. Nevertheless, they are susceptible to SCC (particularly intergranular SCC), whereas most of the ferritic and F/M alloys are not. Moreover, SCC is exacerbated by persistent irradiation damage, i.e. irradiation-assisted SCC (IASCC) [38]. Of these nickel-base alloys, only Incoloy 800H has been qualified for nuclear application up to 760°C under the ASME B&PV Code Subsection NH. However, the swelling resistance of Incoloy 800 is poor and its application at temperatures in the range of 400-650°C will be severely limited by the rapid breakdown in swelling resistance triggered by irradiation-enhanced precipitation of several carbide phases and the co-operative growth of attached cavities [39]. Incoloy 800 develops extensive intergranular and intragranular precipitation of the carbide phases M_6C and $M_{23}C_6$ during thermal aging in the 600-900°C range [40].

6. Internal components

Internal components of the RPV-SCWR include in-core and core-support components such as fuel cladding (discussed above), fuel rod spacers, fuel assembly ducts, control rod guide thimbles, control rod guide tubes, core former, core barrel, and threaded structural fasteners. Under RPV-SCWR operating conditions, the structural materials recommended for both incore and core-support components are primarily F/M steels and low-swelling variants of austenitic stainless steels [9]. The F/M steels of interest are based on 9%Cr-1%Mo such as Grade 91 and a series of reduced-activation alloys in which the Mo and Nb are replaced with W, V, and Ta, such as Japanese F82H and the United States 9Cr-2WVTa alloys. The list also includes Japanese NF616 (P92) and HCM12A (12Cr) and European E911, which were developed for service at 620°C as simple modifications of Grade 91. In addition to corrosion resistance, the other concern about F/M steels is that they lose their strength when exposed to high temperatures for long durations, especially when they are under stress (creep). Consequently, these alloys may not be suitable for the highest temperature locations, in particular for excursions during abnormal conditions. Moreover, there is no experience with F/M steels in currently operating nuclear reactors [9].

In ODS steels, the body centered cubic structure provides the irradiation swelling resistance while the dispersed oxides (e.g., yttria, titania) provide enhanced high-temperature strength.

Incoloy MA-957 (Fe-13Cr-0.26Mo-0.9Ti-0.26 Y_2O_3) successfully survives, with no signs of degradation, conditions significantly more severe than what is expected for the hot SCWR fuel pins in the RPV design, i.e., temperatures up to 650°C, although corrosion in SCW requires investigation [41]. This supports the potential of ODS steel for fuel cladding. Nevertheless, the main issues with all ODS alloys relative to their application in an SCWR are (i) significant uncertainties regarding their compatibility with the SCW coolant, (ii) high cost of fabrication, and (iii) weldability. However, because of their potential, the United States, Japan, and Europe have special programs for development of ODS alloys for nuclear applications and this is an area of focus for the on-going Generation IV program in Canada.

7. **Power conversion system**

In the SCWR, it is expected that the hot coolant at 500-625°C and 25 MPa supplied by the reactor enters the power conversion system, expands through the turbine, is condensed, cleaned, pumped to 25 MPa, and then reheated to 280-350°C before re-entering the reactor. The steam generated in fossil-fuel-fired supercritical steam plants has a temperature range of 540-600°C under pressure of 25-30 MPa. Therefore, there is a well-established manufacturing base for turbines for operation at the supercritical steam conditions of interest in the SCWR, as well as extensive experience in their use (e.g. [42]). Nonetheless, the extent to which the experience from fossil-fuel-fired supercritical steam power plants could be relevant to the SCWR case largely depends on similarities and differences in the quality of the steam and the coolant, in particular, the extent to which the level and types of impurities in the coolant are different from those in fossil-fuel-fired practice.

Problems associated with turbines have caused outages at fossil-fuel-fired and nuclear power plants. The main materials issues related to these outages have involved thermal fatigue cracking of rotors and discs, condensate-related corrosion or stress corrosion cracking of the last stages of the turbine, and solid particle erosion of the first stage guide vanes. The critical design criterion for steam turbine blades is high-cycle fatigue: un-notched for the airfoil area, and notched for the blade root area. Some of the candidate materials for the SCWR power conversion system are Grade 91, Grade 92, Nimonic 80A, Inconel 718, types 403 and 422, Nimonic 90, and M252 [3, 9].

8. Conclusions and remarks

No *nuclear* reactor has yet been built in which supercritical water is the coolant. On the other hand, many fossil-fuel-fired power plants using supercritical water have been built. Moreover, research on new versions of fossil-fuel-fired power plants operating with ultra-supercritical steam has been underway for many years now in the United States, Europe, and Japan. However, there is no precedent for the service conditions that materials in the SCWR core will experience.

Considering only creep, all three classes of materials, i.e., F/M steels, austenitic steels, and nickel-base superalloys, can be potential candidates for out-of-core applications at 625°C and 25 MPa coolant pressure. Creep-fatigue data show that the number of cycles to failure decreases with the introduction of hold time, and the effect is more severe in an oxidizing environment. Additionally, creep-fatigue deformation can be more detrimental to welds than to the base metal. It is noted that the complexity of the SCWR environment, i.e., SCW in the presence of irradiation, is an important concern which affects coolant quality. As a result, the

out-of-core materials could experience oxidizing and/or reducing environments which can degrade their mechanical performance, especially creep-fatigue behavior.

The in-core materials are exposed to neuron irradiation and higher temperatures, in addition to the SCW environment. Because of their well-known creep resistance, nickel-base alloys become more attractive as the service temperature increases. However, commercial nickel-base alloys, e.g. Alloys 617, 800, 625, and Hastelloy X, are susceptible to damaging phenomena related to irradiation-induced segregation, irradiation-enhanced phase instabilities and irradiation-induced helium bubble and void formation. Nevertheless, there have been promising advances in this area. For example, high burn-up levels were achieved with PE-16 (a nickel-base alloy) clad fuel pins in the European fast breeder reactor program through careful fuel pin design where cladding stresses were maintained below the level needed to induce grain boundary helium bubble growth [43]. It is also noted that fuel assemblies are not designed for the lifetime of the reactor and are replaced after a few years in service. This would affect the materials selection for cladding because the clad material is allowed to tolerate a safe level of damage before its service period is ended.

Regarding the austenitic steels, advanced austenitic stainless steels which are resistant to swelling are being considered for in-core applications. D9 alloy is a modified type 316 stainless steel with controlled additions of titanium and silicon, with lower chromium and higher nickel contents. Its resistance to swelling from neutron irradiation, and irradiation creep behavior, are better than those of type 316 stainless steel. D9 is the alloy selected for the fuel cladding for the Prototype Fast Breeder Reactor (PFBR) that is being constructed in India [44]. PNC316 (similar to D9), an austenitic stainless steel containing titanium, niobium, boron, and phosphorous to improve the high temperature creep properties and swelling resistance, has been used as cladding and ducts in Japan's fast breeder reactor (PFBR MONJU).

F/M steels are important candidate materials for the Generation IV nuclear reactors. This is owing to several factors such as high thermal conductivity, low thermal expansion coefficient, resistance to SCC, good weldability, good microstructural stability at high temperature, and better dimensional stability than austenitic steels under irradiation. As a result, they have undergone considerable evolution for nuclear applications over the past few decades. F82H, JLF-1, EUROFER II, and 9Cr-2WVTa (all with chromium contents \leq 9.5) are examples of such development. These conventional steels may not be considered for fuel cladding in the CANDU-SCWR where temperature can rise up to 850°C. Even nickel-base alloys that have been developed for high temperature applications may not survive the irradiation damage in the SCW environment. In this regard, ODS alloys, in which the nano-scale clusters or particles can act as sinks for interstitials and vacancies created by irradiation, have unique potential.

On the other hand, at temperatures below 650°C, conventional and some advanced high temperature steels could be prime candidates. The microstructures of these steels are specially designed to resist creep deformation below 650°C. However, since the microstructure evolves over time, an important criterion for selection would be long-term stability of the microstructure, which controls the long-term high temperature mechanical properties. This would include consideration of possible transformation of metastable phases present in the initial microstructure.

The SCW environment and oxidation also affect the mechanical performance of materials. This is especially important in creep-fatigue. The protective effect of chromium at high temperatures has led to the development of high-chromium steels. However, as stated above, there might be a limit to Cr content above which resistance to oxidation in SCW degrades. Furthermore, 7-9% Cr is favoured in F/M steels for nuclear applications, because higher Cr contents cause embrittlement in F/M steels under irradiation. This could be one of the reasons why many advanced steels developed recently for nuclear applications have low Cr contents, e.g. 3%.

It is obvious that mechanical performance of SCWR materials is critical, especially for the CANDU-SCWR that will operate at higher temperature than the Japanese and European SCWR. The Canadian Generation IV program has dedicated a significant effort in this respect to fulfill Canada's international commitments to the development of SCWR. The Materials Technology Laboratory of Natural Resources Canada is substantially enhancing its capabilities in development and characterization of materials through acquiring state-of-the-art new facilities to investigate high-temperature mechanical properties of nuclear materials and develop ODS alloys for applications in the SCWR. The laboratory has already established several collaborations with universities and research centers, locally and internationally, and would welcome new collaborations.

9. References

- [1]. "A technology roadmap for Generation IV nuclear energy systems", GIF-002-00, Issued by U.S. DOE Nuclear Energy Research Advisory Committee and the Generation IV International Forum, December 2002.
- [2]. Generation IV International Forum (<u>www.gen-4.org</u>).
- [3]. Bill Corwin, *et al.*, "Supercritical water reactor review meeting; materials issues", Oak Ridge National Laboratory, Madison, Wisconsin, April 30, 2003 presentation.
- [4]. Generation IV Roadmap Crosscutting fuels and materials R&D scope report, GIF-010-00, December 2002.
- [5]. B.S. Rodchenkov and A.N. Semenov, "High temperature mechanical behavior of Zr-2.5%Nb alloy", <u>Transactions of the 17th International Conference on Structural</u> <u>Mechanics in Reactor Technology</u>, Prague, Czech Republic, August 17-22, 2003. Paper # C05-1.
- [6]. "Supercritical water reactor (SCWR) Progress report for the FY-03 Generation-IV R&D activities for the development of the SCWR in the U.S.", INEEL/EXT-03-01210, September 2003.
- [7]. CANDU-SCWR, AECL, Information Exchange Meeting, Washington, DC, November 19, 2002.
- [8]. C.K. Chow and H.F. Khartabil, "Conceptual fuel channel design for CANDU-SCWR", *Nuclear Engineering and Technology*, Vol. 40, No. 2, 2008, pp.139-146.
- [9]. J. Buongiorno and P.E. MacDonald, "Supercritical water reactor (SCWR) survey of materials experience and R&D needs to assess viability", Idaho National Engineering and Environmental Laboratory, Bechtel BWXT Idaho, LLC. INEEL/EXT-03-00693, September 2003.

- [10]. R.L. Klueh, "Elevated temperature ferritic and martensitic steels and their application to future nuclear reactors", *International Materials Reviews*, Vol.50, 2005, pp.287-310.
- [11]. D. Gomez Briceno, L. Castro, and F. Blazquez, "Oxidation and stress corrosion cracking of stainless steels in SCWRs", <u>Proceedings of the OECD NEA NSC</u> <u>Workshop on Structural Materials for Innovative Nuclear Systems (SMINS)</u>, Karlsruhe, Germany, 2007, June 4-6.
- [12]. C. Fazio, *et al.*, "European cross-cutting research on structural materials for Generation IV and transmutation systems", *Journal of Nuclear Materials*, Vol. 392, 2009, pp.316-323.
- [13]. P.J. Ennis and A. Czyrska-Filemonowics, "Recent advances in creep resistant steels for power plant applications", *OMMI Internet Journal*, Vol. 1, No. 1, 2002, pp.1-28.
- [14]. S. Caminada, *et al.*, "Ferritic and austenitic grades for new generation of steam power plants", <u>Proceedings of the Fifth International Conference on Advances in Materials</u> <u>Technology for Fossil Power Plants</u>, Marco Island, Florida, 2007, October 3-5, pp.564-581.
- [15]. Y. Takahasi, "Study on creep-fatigue evaluation procedures for high-chromium steels. Part I: test results and life prediction based on measured stress relaxation", *International Journal of Pressure Vessels and Piping*, Vol. 85, 2008, pp.406-442.
- [16]. B. Fournier, *et al.*, "Creep-fatigue-oxidation interactions in a 9Cr-1Mo martensitic steel. Part I: effect of tensile holding period on fatigue lifetime", *International Journal of Fatigue*, Vol. 30, 2008, pp.649-662.
- [17]. B. Fournier, *et al.*, "Creep-fatigue-oxidation interactions in a 9Cr-1Mo martensitic steel. Part II: effect of compressive holding period on fatigue lifetime", *International Journal of Fatigue*, Vol. 30, 2008, pp.663-676.
- [18]. ASME Boiler and Pressure Vessel Code, Section III, Division 1– Subsection NH, Class 1 Components in Elevated Temperature Service, ASME 2005, 2005 Addenda, July 1, 2005.
- [19]. R.L. Klueh, J-J. kai, and D.J. Alexander, "Microstructural-mechanical properties correlation of irradiated conventional and reduced-activation martensitic steels", *Journal of Nuclear Materials*, Vol. 225, No. 1-3, 1995, pp.175-186.
- [20]. P.J. Maziasz, R.L. Klueh, and J.M. Vitek, "Helium effects on void formation in 9Cr-1MoVNb and 12Cr-1MoVW irradiated in HFIR", *Journal of Nuclear Materials*, Vols. 141-143, Part 2, November-December 1986, pp.29-937.
- [21]. D.S. Gelles, "Microstructural development in reduced activation ferritic alloys irradiated to 200 dpa at 420°C", *Journal of Nuclear Materials*, Vols. 212-215, Part 1, September 1994, pp.714-719.
- [22]. R.L. Klueh and J.M. Vitek, "Elevated-temperature tensile properties of irradiated 9Cr-1MoVNb steel", *Journal of Nuclear Materials*, Vol.132, 1985, pp.27-31.

- [23]. D.S. Gelles, "Microstructural examination of commercial ferritic alloys at 200 dpa", *Journal of Nuclear Materials*, Vols. 233-237, No.1-3, 1996, pp.293-298.
- [24]. R.L. Klueh and J.M. Vitek, "Fluence and helium effects on the tensile properties of ferritic steels at low temperatures", *Journal of Nuclear Materials*, Vol.161, No.1, 1989, pp. 13-23.
- [25]. R.L. Klueh and J.M. Vitek, "Tensile properties of 9Cr-1MoVNb and 12Cr-1MoVW steels irradiated to 23 dpa at 390-550°C", *Journal of Nuclear Materials*, Vol.182, 1991, pp.230-239.
- [26]. C. Wassilew, K. Herschbakh, E. Materna-Morris, and K. Elhrich, "Irradiation behavior of 12% chromium martensitic steels", <u>Proceedings of the conference on Ferritic Alloys for Use in Nuclear Energy Technologies</u>, Snowbird, Utah, June 19-23, 1983. The Metallurgical Society of AIME, Warrendale, Pa, 1984, pp.607-614.
- [27]. R.L. Klueh and D.J. Alexander, "Embrittlement of 9Cr-1MoVNb and 12Cr-1MoVW steels irradiated in HFIR", *Journal of Nuclear Materials*, Vol.187, 1992, pp.60-69.
- [28]. R.L. Klueh, D.J. Alexander, and E.A. Kenik, "Development of low-chromium, chromium-tungsten steels for fusion", *Journal of Nuclear Materials*, Vol.227, No.1-2, 1995, pp.11-23.
- [29]. R.L. Klueh, D.J. Alexander, and P.J. Maziasz, "Bainitic chromium-tungsten steels with 3% chromium", *Metallurgical and Materials Transactions A*, Vol.28A, No.2, 1997, pp.335-345.
- [30]. R.J. Stofanak and K. Matuszuk, "Irradiation embrittlement behavior of high strength low alloy steels containing about 3.3% nickel", <u>Proceedings of the Tenth International</u> <u>Conference on Environmental Degradation of Materials in Nuclear Power Systems –</u> <u>Water Reactors</u>, The Minerals, Metals and Materials Society, Warrendale, PA, 2001, 14 pages.
- [31]. G.L. Wire, W.J. Beggs, and T.R. Leax, "Evaluation of irradiation embrittlement of A508 Gr 4N and comparison to other low-alloy steel", *ASTM Special Technical Publication*, 1447, 2004, pp.179-193.
- [32]. "Effects of nickel on irradiation embrittlement of light water reactor pressure vessel steels", International Atomic Energy Agency (IAEA), IAEA-TECDOC-1441, June 2005.
- [33]. N. Boukis, N. Claussen, K. Ebert, R. Janssen, and M. Schacht, "Corrosion screening tests of high-performance ceramics in supercritical water containing oxygen and hydrochloric acid", *Journal of the European Ceramic Society*, Vol.17, No.1, 1997, pp.71-76.
- [34]. B. Savoini, D. Cáceres, I. Vergara, R. González, and J. E. Muñoz Santiuste, "Radiation damage in neutron-irradiated Yttria-Stabilized-Zirconia single crystals", *Journal of Nuclear Materials*, Vol.277, No.2-3, 2000, pp.199-203.
- [35]. C.K. Chow and H.F. Khartabil, "Fuel channel design for CANDU-SCWR", Presentation at SCWR-2007, Shanghai, China, March 12-17, 2007.

- [36]. G.R. Odette, M.J. Alinger, and B.D. Wirth, "Recent developments in irradiation-resistant steels", *Annual Review of Materials Research*, Vol. 38, 2008, pp. 471-503.
- [37]. Y. Guerin, G.S. Was, and S.J. Zinkle, "Materials challenges for advanced nuclear energy systems", *MRS Bulletin*, Vol.34, January 2009, pp.10-14.
- [38]. C. Cabet, J. Jang, J. Konys, and P.F. Tortorelli, "Environmental degradation of materials in advanced reactors", *MRS Bulletin*, Vol.34, January 2009, pp.35-39.
- [39]. A.F. Rowcliffe, L.K. Mansur, D.T. Hoelzer, and R.K. Nanstad, "Perspectives on radiation effects in nickel-base alloys for applications in advanced reactors", *Journal of Nuclear Materials*, Vol.392, 2009, 341-352.
- [40]. K.Bhanu Sankara Rao, H. Schuster, and G.R. Halford, "On massive carbide precipitation during high temperature low cycle fatigue in alloy 800H", *Scripta Metallurgica et Materialia*, Vol.31, No.4, 1994, pp.381-386.
- [41]. J. Bottcher, S. Ukai, and M. Inoue, "ODS steel clad MOX fuel-pin fabrication and irradiation performance in EBR-II", *Journal of Nuclear Technology*, Vol.138, No.3, 2002, pp.238-245.
- [42]. R. Viswanathan, D. Gandy, and K. Coleman, (edits.), <u>Proceedings of the Fifth</u> <u>International Conference on Advances in Materials Technology for Fossil Power</u> <u>Plants</u>, Marco Island, Florida, October 3-5, 2007
- [43]. A.F. Rowcliffe, *et al.*, "Perspectives on radiation effects in nickel-base alloys for applications in advanced reactors", *Journal of Nuclear Materials*, Vol.392, 2009, pp.341-352.
- [44]. "Design of prototype fast breeder reactor", Indira Gandhi Centre for Atomic Research, Kalpakkam-603 102, December 2003.