MICROSTRUCTURAL CHARACTERIZATION AND MECHANICAL PROPERTIES OF EXCEL ALLOY PRESSURE TUBE MATERIAL

by

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Abstract

Microstructural characterization and mechanical properties of Excel (Zr-3.5%Sn-0.8%Mo-0.8%Nb), a dual phase $\alpha$Zr-hcp and $\beta$Zr-bcc pressure tube material, is discussed in the current study which is presented in manuscript format. Chapter 3 discusses phase transformation temperatures using different techniques such as quantitative metallography, differential scanning calorimetry (DSC), and electrical resistivity. It was found that the $\alpha$Zr $\rightarrow$ $\alpha$Zr+ $\beta$Zr and $\alpha$Zr+ $\beta$Zr $\rightarrow$ $\beta$Zr transformation temperatures are in the range of 600-690°C and 960-970°C respectively. Also it was observed that upon quenching from temperatures below ~860°C the martensitic transformation of $\beta$Zr to $\alpha'$-hcp is halted and instead the microstructure transforms into retained $\beta$Zr with $\omega$ hexagonal precipitates inside $\beta$Zr grains. Chapter 4 deals with aging response of Excel alloy. Precipitation hardening was observed in samples water-quenched from high in the $\alpha$Zr+$\beta$Zr or $\beta$Zr regions followed by aging. The optimum aging conditions were found to be 450°C for 1 hour. Transmission electron microscopy (TEM) showed dispersion of fine precipitates (~10nm) inside the martensitic phase. Energy dispersive X-ray spectroscopy (EDS) showed the chemical composition of precipitates to be Zr-30wt%Mo-25wt%Nb-2wt%Fe. Electron crystallography using whole pattern symmetry of the convergent beam electron diffraction (CBED) patterns together with selected area diffraction (SAD) polycrystalline ring patterns, suggests the $-6m2$ point group for the precipitates belonging to hexagonal crystal structure, with $a=2.936$ Å and $c=4.481$ Å, i.e. $c/a=1.526$.

Crystallographic texture and high temperature tensile properties as well as creep-rupture properties of different microstructures are discussed in Chapter 5. Texture analysis showed that solution treatment high in the $\alpha$Zr+$\beta$Zr or $\beta$Zr regions followed by water quenching or air cooling results in a more random texture compared to typical pressure tube texture. Variant selection was observed upon water quenching while partial memory effect and some transformation texture
with variant selection was observed in the air-cooled sample. The results of creep-rupture tests suggest that fully martensitic and aged microstructure has better creep properties at high stress levels (>700 MPa) while the microstructure from air cooling from high in the $\alpha_{Zr}+\beta_{Zr}$ region is less sensitive to stress and shows better creep properties compared to the as-received annealed microstructure at lower stresses (<560 MPa).
Co-Authorship

This dissertation is based on the following three manuscripts which are submitted or will be submitted for publication:

Chapter 3

Chapter 4

Chapter 4

The work presented in this dissertation is original and my own with co-authors acting in an advisory capacity.
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Glossary

\( \sigma_0 \) friction stress in Hall-Petch equation

\( \cdot \varepsilon_a \) creep rate in the axial direction of the pressure tube

\( \cdot \varepsilon_t \) creep rate in the transverse direction of the pressure tube

\( \varepsilon_a \) total strain in the axial direction of the pressure tube

\( \varepsilon_t \) total strain in the transverse direction of the pressure tube

\( \tilde{D}_0 \) chemical diffusion constant

\( a \) hexagonal lattice parameter in the basal plane

\( B \) proportionality constant in creep rate equation

\( b \) Burgers vector

\( C \) Heat capacity

\( c \) hexagonal lattice parameter normal to the basal plane

CANDU® CANada Deuterium Uranium reactors

CBED convergent beam electron diffraction

\( C_i \) Concentration of element \( i \) in an alloy

\( CX \) Zr-3.2%Sn-1.1%Nb-1.1%Mo

\( d \) Atomic interplanar spacing

DAD Diffusional Anisotropy Difference

DIC Digital Image Correlation

DSC Differential Scanning Calorimetry

\( E \) Elastic modulus
<table>
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<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>EBSD</td>
<td>electron backscatter diffraction</td>
</tr>
<tr>
<td>EBSP</td>
<td>electron backscatter pattern</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>$e_f$</td>
<td>strain at fracture</td>
</tr>
<tr>
<td>EMPA</td>
<td>electron micro-probe analysis</td>
</tr>
<tr>
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<td>resolved volume fraction of basal pole normals in the axial direction of the pressure tube</td>
</tr>
<tr>
<td>$f_r$</td>
<td>resolved volume fraction of basal pole normals in the radial direction of the pressure tube</td>
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<tr>
<td>$f_t$</td>
<td>resolved volume fraction of basal pole normals in the transverse direction of the pressure tube</td>
</tr>
<tr>
<td>$G$</td>
<td>shear modulus</td>
</tr>
<tr>
<td>$G_d$</td>
<td>Growth anisotropy factor</td>
</tr>
<tr>
<td>GSAS</td>
<td>general structure analysis system</td>
</tr>
<tr>
<td>HEC</td>
<td>high efficiency channel</td>
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<tr>
<td>HV</td>
<td>Vickers hardness</td>
</tr>
<tr>
<td>$I_i$</td>
<td>measured EDS X-ray intensity of element $i$ in an alloy</td>
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<tr>
<td>$k$</td>
<td>Hall-Petch coefficient</td>
</tr>
<tr>
<td>$k$</td>
<td>thermal conductivity</td>
</tr>
<tr>
<td>$k$</td>
<td>magnitude of the electron wave vector</td>
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<td>$k_{AB}$</td>
<td>Cliff-Lorimer factor in TEM quantitative EDS equation</td>
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<tr>
<td>$M$</td>
<td>Taylor factor</td>
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<tr>
<td>$M_f$</td>
<td>Martensite finish temperature</td>
</tr>
<tr>
<td>MPT</td>
<td>micro-pressure tube</td>
</tr>
<tr>
<td>$M_s$</td>
<td>Martensite start temperature</td>
</tr>
<tr>
<td>$n$</td>
<td>stress exponent in creep rate equation</td>
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</tbody>
</table>
Q  activation energy
R  thermal resistance
R  universal gas constant
REC re-entrant channel
SAD selected area diffraction
SCWR super critical water reactor
SEM scanning electron microscope(y)
SIPA stress-induced preferred absorption
SIPN stress-induced preferred nucleation
STEM scanning transmission electron microscope(y)
TC(α, β) Texture Coefficient at α and β
TEM transmission electron microscope(y)
UTS ultimate tensile strength

\( V_i \) Volume fraction of grains having basal poles at an angle \( \alpha \) to a specific direction of the pressure tube

\( \alpha \) azimuth angle on a pole figure

\( \alpha' \) \( \alpha' \) zirconium martensite phase with hcp crystal structure

\( \alpha'' \) \( \alpha'' \) zirconium martensite phase with orthorhombic crystal structure

\( \alpha_{Zr} \) \( \alpha \) zirconium phase with hcp crystal structure

\( \beta \) polar angle on a pole figure

\( \beta_{Ti} \) \( \beta \) titanium phase with bcc crystal structure

\( \beta_{Zr} \) \( \beta \) zirconium phase with bcc crystal structure

\( \theta_B \) Bragg’s angle

\( \lambda \) wavelength

\( \lambda \) inter-particle spacing
\( \rho \) \hspace{1cm} \text{electrical resistivity}

\( \sigma_y \) \hspace{1cm} \text{yield stress}

\( \psi_0 \) \hspace{1cm} \text{electron wave amplitude}

\( \omega_s \) \hspace{1cm} \omega \text{ start temperature}

\( \omega_{Zr} \) \hspace{1cm} \omega \text{ zirconium phase with hexagonal (P6/mmm) crystal structure}
Chapter 1
Introduction

1.1 Zirconium in the Nuclear Industry

Zirconium alloys are one of the major structural materials for components in the core of nuclear reactors. These components are mostly in the form of tubes of different size ranges for applications such as fuel sheathing, guide tubes/calandria tubes, and pressure tubes [1]. A combination of low neutron capture cross-section, high strength, and good corrosion resistance in water makes zirconium alloys the main choice for nuclear applications [2][3].

Zirconium alloys can be categorized into two classes: single phase $\alpha_{Zr}$ alloys such as Zircaloys, and dual phase $\alpha_{Zr}+\beta_{Zr}$ alloys such as Zr-2.5Nb and Excel [4]. Zircaloys with Sn, Fe, Ni, and O as alloying elements were first used as pressure tubes in CANDU reactors and are currently used as fuel cladding and calandria tubes. Dual phase Zr-2.5Nb alloy is the current material for CANDU pressure tubes. Zr-1%Nb is used as fuel cladding in Russian reactors [1][2][5].

1.2 Motivation

The thermal efficiency of CANDU reactors can be increased by increasing the coolant temperature, for example in the conceptual design of the Generation IV Super Critical Water CANDU reactor (CANDU-SCWR) a thermal efficiency of up to 40% can be achieved by increasing the coolant temperature from 300°C (current generation) to
This is accomplished by using a re-entrant fuel channel design that requires the pressure tube to operate at 400°C [6][7]. This implies the need for a more creep resistant material for the pressure tube than the currently used Zr-2.5Nb alloy. The aim of this research is to study and characterize the microstructure and its correlation with mechanical properties in particular creep-rupture of the zirconium alloy Excel. This alloy is the candidate material for the Generation IV Super Critical Water CANDU reactor (CANDU-SCWR). This work serves as the initial and fundamental steps in characterization of Excel in the heat treated conditions and provides the basic essential microstructural information for further assessment of this alloy.

This dissertation is presented in a manuscript format comprised of three parts. Part I (Chapter 3) discusses the phase transformation temperatures and phase transformation behaviour of Excel. In order to design any thermal/thermo-mechanical treatment to achieve certain mechanical properties it is necessary to know the phase diagram and the transformation temperatures of the studied system. Since there is no published phase diagram for the Excel alloy or any data on phase transformation temperatures, different methods such as water-quenching followed by quantitative metallography, differential scanning calorimetry (DSC), and electrical resistivity measurement were employed to study the alloy’s transformation temperatures. The microstructure and solute atom distribution at different temperatures were also studied.

In part II (Chapter 4) the aging response and characterization of precipitates in the Excel alloy is discussed. Knowing the approximate phase transformation temperatures and volume fraction of each phase at different temperatures, heat treatments were performed
to assess the precipitation hardening of Excel. The microstructure and precipitates were characterized by analytical transmission electron microscopy techniques.

Finally part III (Chapter 5) reports the effect of different heat treatments on texture as well as high temperature tensile and creep-rupture properties of the Excel alloy. The crystallographic texture and microstructure of different heat treatments that were developed in Chapter 4 are studied in Chapter 5. Variant selection based upon phase transformation is discussed. High temperature tensile tests and creep rupture experiments were conducted to study the creep resistance of different microstructures of Excel.

Most of the experimental techniques that are used in this study are explained in Chapter 2 (Literature Review). Any other experimental techniques not covered in Chapter 2 are explained in detail in the relevant chapter.
1.3 References

**Chapter 2**  
**Literature Review**

Zirconium alloys are the main structural materials in the core of nuclear reactors. They are used mostly in the form of tubes for three main applications: fuel sheathing, guide/calandria tubes and pressure tubes [1]. In the CANDU design, the reactor core consists of a calandria vessel inside which individual horizontal fuel channels are located. The fuel channel inside which the nuclear reaction takes place, consists of a pressure tube, which contains fuel bundles and high pressure heavy water coolant, a calandria tube which is concentric with the pressure tube, and two end fittings (Figure 2-1) [2][3].

![Figure 2-1 Schematic diagram of CANDU fuel channel](image)

Low neutron capture cross section is a key requirement for materials that make up CANDU reactor’s core components. Zirconium and its alloys are the only materials that
satisfy this requirement and meet the minimum strength and corrosion requirements for CANDU reactors [4].

Pressure tubes are subjected to high stress and high temperature from the high pressure coolant and the weight of the fuel and coolant. In the current CANDU reactors the coolant pressure is 9.5-11 MPa with a temperature of 250°C and 278-312°C at the inlet and outlet, respectively [3][5]. The high pressure coolant introduces stresses in the axial and transverse direction of the tube with the ratio of approximately 1:2 (65 MPa and 130 MPa, respectively). Also the weight of the fuel bundles and coolant cause the pressure tube to sag [2].

The first generation of CANDU reactor pressure tubes were made from Zircaloy-2 (Zr-1.2-1.7% Sn- 0.07-0.2% Fe- 0.05-0.15% Cr- 0.03-0.08%Ni), a single phase $\alpha_{Zr}$-hcp alloy [6][7]. However the current pressure tube material is Zr-2.5Nb in the cold-worked condition (27%). It is a dual phase alloy $\alpha_{Zr}$-hcp and $\beta_{Zr}$-bcc (<10% volume fraction) [8] with better creep resistance and higher strength than Zircaloy-2 and a crystallographic texture consisting of the basal pole normals mostly in the transverse direction. This material gives quite satisfactory properties for the current working conditions within a CANDU reactor [3][9].

The in-service life limiting factors of the pressure tubes are dimensional changes due to irradiation growth, irradiation creep and thermal creep, corrosion and hydrogen ingress, and change in mechanical properties due to irradiation [10].

Irradiation-creep as well as thermal-creep, particularly at high pressures and temperatures encountered in the outlet region of the pressure tubes is most likely the main life limiting factor in pressure tubes. This creep deformation causes expansion of the pressure tube in
the transverse, circumferential, direction resulting in the coolant to bypass the fuel and thus results in the reduction of the thermal efficiency of the reactor. Also creep might cause sagging of the pressure tube to the extent that it touches the calandria tube. Furthermore, due to the anisotropy of the pressure tube, irradiation growth and creep cause axial expansion of the tube. This could result in the tube interference with feeder pipes. However, such axial expansion can be accommodated, to some extent, through the allowed movement of the end fittings [3][11].

It is possible to increase the thermal efficiency of CANDU reactors by increasing the coolant temperature. This is the goal in the design of the Generation IV CANDU Super Critical Water Reactors, CANDU-SCWR. This design is based on super critical water coolant at a pressure of 25 MPa with an inlet and outlet temperature of 350°C and up to 625°C, respectively. This corresponds to a thermal efficiency of 48%, compared to 29% in the current CANDU reactor design [12][13].

2.1 Zirconium Alloy Excel and Binary Phase Diagrams

The zirconium alloy Excel (Zr-3.5%Sn-0.8%Mo-0.8%Nb) [11] in annealed condition, developed for the current generation of CANDU reactors, is a dual phase, α-hcp and β-bcc material. At room temperature the major micro-constituent of Excel is α-hcp with the unstressed lattice parameters of \( a=3.2316 \text{ Å} \) and \( c=5.1475 \text{ Å} \). The minor phase in the microstructure is β-bcc with the lattice parameter of \( 3.6090 \text{ Å} \) [14].

The range of chemical composition of the alloying elements and impurities is as follows: 3.2-3.8% Sn, 0.6-1% Mo, 0.6-1% Nb, 0.15% Fe, and 0.09-0.16% O. Among these, Sn

\[ \text{lattice parameters are for pure Zr} \]
and O are $\alpha_{Zr}$-stabilizing elements dissolving mostly in the $\alpha_{Zr}$-phase, when heated into the $\alpha_{Zr}+\beta_{Zr}$ phase field, increasing the $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ transformation temperature [15]. It has been reported that addition of 1\%Sn in the Zr-3\%Nb-1\%Sn system has two major effects: 1) increasing the $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ transus temperature by 28°C; 2) lowering the solubility of Nb in $\alpha_{Zr}$ [16]. Mo, Nb, and Fe are $\beta_{Zr}$-stabilizers concentrating in the $\beta$-phase and lowering the $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ transformation temperature [14][17].

Binary Zr-Sn, Zr-Mo, and Zr-Nb phase diagrams are shown in Figures 2-2 to 2-4.

Figure 2-2 Zr-Sn binary phase diagram [18]
Figure 2-3 Zr-Mo binary phase diagram [19]

Figure 2-4 Zr-Nb binary phase diagram [20]
Figure 2-5 shows isothermal sections of the Zr-Nb-Sn ternary phase diagram at 500°C and 725°C.

According to the binary phase diagrams of Zr-Sn, Zr-Mo, and Zr-Nb, Excel alloy has the potential for precipitation hardening. Zr-Sn binary system exhibits a peritectoid reaction at 953°C, $\text{Zr}_4\text{Sn} + \beta_{\text{Zr}} \rightarrow \alpha_{\text{Zr}}$, and therefore, theoretically speaking, it should be possible to get precipitation of $\text{Zr}_4\text{Sn}$ [18][22][23]. Also the Zr-Nb-Sn ternary phase diagram (Figure 2-5) shows the presence of $\text{Zr}_4\text{Sn}$ phase. However there is some discrepancy in the literature regarding precipitation of $\text{Zr}_4\text{Sn}$ or any tin-rich particles. While Douglas [21] reported a considerable increase in tensile strength of Zr-0.5%Nb-3%Sn alloy as a result of precipitation of $\text{Zr}_4\text{Sn}$ by up to 33% volume fraction, Carpenter et al. [24] found that there is no precipitation in Zr-Sn alloys with less than 9% Sn, and even at higher concentrations of Sn there is very little or no hardening effect. In a recent reassessment of the Zr-Sn binary system Toffolon et al. [25] found that the solubility of Sn in $\alpha_{\text{Zr}}$ is 8.2% and 6.9% at 900°C and 600°C respectively which is in agreement with the study of
Carpenter et al. [24]. Pérez and Toffolon et al. [26] then proposed new solvus lines for the Zr-Sn binary phase diagram which suggests the solubility of Sn in $\alpha_{Zr}$ to be about 6.4% at room temperature. They also proposed a lower temperature (943±5°C) for the peritectoid $Zr_4Sn + \beta_{Zr} \rightarrow \alpha_{Zr}$ reaction.

The Zr-Mo binary system has the $\beta_{Zr} \rightarrow \alpha_{Zr} + Mo_2Zr$ eutectoid reaction at 738°C which gives the potential for age hardening by precipitation of the $Mo_2Zr$ intermetallic phase [19].

The pseudo-ternary Zr-Nb-Fe (1200 ppm O) phase diagram with iron content varying from 150 wt. ppm to 5000 wt. ppm was studied by Toffolon et al. [27] who showed the presence of Zr-Nb-Fe intermetallic phase in the microstructure of alloys containing more than 0.3%Nb. The composition of this phase is 35%Zr-35%Nb-30%Fe with a hexagonal crystal structure. Furthermore they found that addition of Sn up to 2% has no effect on the composition of the precipitates or phase diagram boundaries.

2.2 Fabrication, Microstructure, and Texture of Pressure Tubes

The current fabrication route for CANDU reactor pressure tubes is as follows: 1) forging the ingots of approximately 3500mm in length $\times$ 580mm in diameter into two logs of approximately 2800mm in length $\times$ 210 mm in diameter; 2) machining the logs to produce hollow billets of approximately 560mm long $\times$ 195mm diameter; 3) extrusion of the billets at 815°C at an extrusion ratio of 11:1; 4) 27% cold-working to produce tubes of approximately 112mm OD and 104mm ID; 5) stress relieving at 400°C for 24 hr [28][29][30].
This fabrication route results in a microstructure consisting of α\textsubscript{Zr} grains elongated in the axial direction and flattened and folded in the radial-transverse plane. The thickness of the grains is in the range of 200-300 nm for pressure tubes made from water-quenched billets and 500-1000 nm for the tubes made from furnace-cooled billets. The β\textsubscript{Zr}-phase forms a continuous film along the grains boundaries of α\textsubscript{Zr} grains \[31\].

CANDU pressure tubes have a strong crystallographic texture with most of the grains oriented with their basal plane normals in the transverse-radial plane and biased towards the transverse direction of the tube and sometimes with a weak component in the axial direction \[32\]. The texture of pressure tubes is established during the extrusion process and the cold-drawing step has little effect on the final texture. Cheadle et al. \[33\] studied factors that might affect the microstructure and texture of pressure tubes and found that microstructure of the billet has no effect on the texture and only determines the size of the α\textsubscript{Zr} grain. The percentage of α\textsubscript{Zr}-phase in the α\textsubscript{Zr}+β\textsubscript{Zr} region, which is determined by the extrusion temperature, was found to have very little effect on the texture; however extrusion in the β\textsubscript{Zr}-phase results in an α\textsubscript{Zr}-phase texture inherited from the high temperature β-phase texture through Burgers orientation relationship \[34\] with a Widmanstätten microstructure. According to Holt and Aldridge \[35\] who studied the effect of extrusion ratio and temperature on the texture of Zr-2.5Nb pressure tubes, by increasing the extrusion ratio from 4:1 to 9:1, the ratio of basal normals in the radial direction to that in the transverse direction decreases; also the concentration of basal plane normals in the axial direction decreases by increasing the extrusion ratio. Increasing the extrusion temperature causes an increase in the concentration of basal plane normals in the axial direction as well as a decrease in the ratio of basal plane
normals in the radial direction to that in the transverse direction. The $\alpha_{Zr}$ grain size of the billet has a similar effect to extrusion temperature, i.e. shifting the basal plane normals towards the transverse direction in the radial-transverse plane which is contrary to the study of Cheadle et al. [33] who reported no effect of billet grain size on texture, however the extrusion ratio in their study was higher than Holt and Aldridge's study [35], 16:1 compared to 9:1.

In a study of microstructure and micro-texture of extruded Zr-2.5Nb pressure tubes Holt and Zhao [32] found that the three components of the texture of pressure tubes, i.e. axial, radial, and transverse, correlate with $\alpha_{Zr}$ grains morphology and their dislocation substructure. In the axial-radial cross-section, elongated $\alpha_{Zr}$ grains with high density of $a$ and $c+a$ dislocations and $c$ axis oriented at a high angle to the long dimension of $\alpha_{Zr}$ grains, correspond to the texture component with the $c$ axis in the radial-transverse plane biased towards the radial direction. Elongated $\alpha_{Zr}$ grains with low dislocation density and $c$ axis close to the long dimension of $\alpha_{Zr}$ grains, correspond to the texture component with the $c$ axis in the radial-transverse plane, predominantly in the transverse direction. Finally the axial component of texture corresponds to low dislocation density Widmanstätten-like $\alpha_{Zr}$ grains that are transformed from $\beta_{Zr}$-phase. The radial component of texture which occurs at relatively low extrusion temperatures is due to pyramidal ($c+a$) slip. The transverse component which occurs at relatively high extrusion temperatures is associated with the high temperature $\beta_{Zr}$-phase texture, effect of stress on $\alpha_{Zr}/\beta_{Zr}$ phase transformation, and grain boundary sliding. Finally the axial component in texture which occurs at high temperatures is associated with the high temperature $\beta_{Zr}$-phase texture and high volume fraction of $\beta_{Zr}$-phase present during extrusion [31].
The studied Excel alloy pressure tube is fabricated through a hot extrusion process at a temperature of ~850°C and an extrusion ratio of 10:1. The pressure tube was cold-worked about 25% and annealed at about 750°C, which is low in the $\alpha_{\text{Zr}} + \beta_{\text{Zr}}$ region, and finally it was stress relieved at 400°C for 24 hours.

The microstructure of the pressure tube in the annealed condition consists of relatively equiaxed $\alpha_{\text{Zr}}$ grains with the $\beta_{\text{Zr}}$ phase along grain boundaries and at grain corners.

Figure 2-6 shows the (0001) and (110) pole figures of the $\alpha_{\text{Zr}}$ and $\beta_{\text{Zr}}$ phases of the studied Excel pressure tube.

![Figure 2-6 Pole figures of the studied Excel pressure tube a) (0001) $\alpha_{\text{Zr}}$-phase b) (110) $\beta_{\text{Zr}}$-phase](image)

**2.3 Thermal Creep**

Creep is defined as deformation of material under relatively low constant stress (well below yield stress) at elevated temperatures and over a long period of time. To define more precisely what is meant by elevated temperature, creep temperature is often expressed as homologous temperature, i.e. the ratio of test temperature to the melting temperature of the material. Generally, creep comes into consideration at homologous...
temperatures higher that 0.5 [36]. Creep behaviour is usually represented by a plot of strain vs. time (Figure 2-7).

![Figure 2-7 Typical creep curve. Curve A, constant load; Curve B, constant stress [36]](image)

The slope of this curve is referred to as the creep rate (\( \frac{d\varepsilon}{dt} \text{ or } \dot{\varepsilon} \)). The creep curve is usually subdivided into three regimes: 1) transient or primary region which follows the instantaneous non-creep strain (\( \varepsilon_0 \)). In this region the creep rate decreases until a minimum steady-state creep rate is reached. 2) steady-state creep in which the creep rate is constant, and minimum, predominates the major portion of the lifetime. 3) tertiary creep is the region of the creep curve in which the creep rate increases rapidly until failure occurs. The last regime is only observed in constant load creep tests (not in constant stress) and it is associated with severe microstructural degradation such as creep cavitation, cavity linkage and oxidation [36][37].
2.3.1 Creep Deformation Mechanisms

Dislocation Glide

Deformation by this mechanism occurs at low temperatures and high stresses compared to those encountered in creep. The deformation rate depends on the presence of obstacles, i.e. impurities, precipitates, solute atoms and dislocation forests, against dislocation movement and the ease with which dislocations can overcome these barriers.

If there was no barrier, the velocity of dislocations (which together with the number of moving dislocations, determines the macroscopic strain rate) would reach the speed of sound in the material. The strain rate is given by the general formula:

\[ \dot{\gamma} = \dot{\gamma}_0 \exp\left(-\frac{\Delta F}{kT}\right) \left(1 - \frac{\sigma}{\tau}\right) \]

Shear strain rate \(\dot{\gamma}\)

\[ \varepsilon = \varepsilon_0 \exp\left(-\frac{Gb}{kT}\cdot ba\right) \]

Tensile strain rate \(\varepsilon\)

where \(\Delta F\) is the activation energy required to pass an obstacle, \(\tau\) is the flow stress at 0K which reflects the inherent resistance of lattice to dislocation movement (or Peierls stress), \(\dot{\gamma}_0\) is a constant, \(\sigma\) is shear stress, \(G\) is shear modulus, \(b\) is Burger’s vector, \(l\) is the obstacle spacing, \(a\) is activation area, and \(\varepsilon_0\) is a constant [38].

Dislocation Creep

This type of deformation occurs at intermediate to high stresses and homologous temperatures above 0.3-0.5 and involves the glide of dislocations controlled by vacancy
diffusion. The movement of dislocations is hindered by obstacles. However at elevated
temperatures they can pass the barriers by a diffusion-aided process called climb. In this
mechanism the creep rate obeys a power-law equation in the general form of:

$$\dot{\varepsilon}_s = \frac{AD_iGb}{kT} (\frac{\sigma}{G})^n$$  \hspace{1cm} (3)

where $A$ and $n$ (which has the value of 3-8 or most common 5) are materials constant and
$D_i$ is the lattice diffusion coefficient.

Since the diffusion coefficient, $D$, is given by the equation:

$$D = D_0 \exp(-\frac{Q}{kT})$$  \hspace{1cm} (4)

where $D_0$ is diffusion constant and $Q$ is the activation energy, then equation (3) can be
rewritten as [37][38]:

$$\dot{\varepsilon}_s = B\sigma^n \exp(-\frac{Q}{kT})$$  \hspace{1cm} (5)

**Diffusion Creep**

This mechanism becomes active at high temperatures and low stresses ($\frac{\sigma}{G} \langle 10^{-4}\rangle$. This
type of flow involves the stress-directed diffusion of atoms. Here, “stress-directed”
means that there is a flow of vacancies from grain boundaries experiencing tensile stress
towards those under compressive stress; and simultaneously there is a flow of atoms in
the opposite direction [36][37].

Diffusion creep can be divided into two distinct mechanisms on the basis of diffusion
path.
If diffusion occurs through the grains, it is called Nabarro-Herring creep and can be represented by the equation:

\[ \varepsilon_s \approx \frac{14\sigma b^3 D_v}{kTd^2} \]  

(6)

where \( d \) is grain size and \( D_v \) is lattice diffusion coefficient.

At lower temperatures where diffusion along grain boundaries is dominant, the flow mechanism is called Coble creep which is given by equation:

\[ \varepsilon_s \approx \frac{50\sigma b^4 D_{gb}}{kTd^3} \]  

(7)

where \( D_{gb} \) is grain boundary diffusion coefficient [36].

### 2.3.2 Thermal Creep of Zirconium Alloys

The steady state creep rate of metals usually increases exponentially with temperature and in the stress range of \( 5 \times 10^{-6} < \sigma / G < 10^{-3} \) (\( G \) is the shear modulus) it has a power law dependence on stress, thus it can be expressed in the general form of [36][39]:

\[ \varepsilon = B\sigma^n \exp(-\frac{Q}{RT}) \]  

(8)

where \( B \) is a constant, \( n \) is the stress exponent, \( Q \) is the apparent activation energy, and \( R \) is the gas constant.

In a study of Zr-2.5Nb fuel cladding Kohn [40] reported a stress exponent of 5.3 and an activation energy of 265 KJ/mol in the temperature range of 350°C (at stresses higher than 160 MPa) to 450°C (at stresses higher than 60 MPa). Christodoulou et al. [41] reported a stress exponent value of 4 for Zr-2.5Nb pressure tube material in the temperature range of 100-323°C and stresses up to 450 MPa. According to the literature
survey in Reference [41] the stress exponent for Zr alloys for creep rates lower than $5 \times 10^{-7} \, \text{h}^{-1}$ ($\sim 1 \times 10^{-9} \, \text{s}^{-1}$) is lower than 5. In a study of five different Zr-Sn-Mo alloys and CX alloy (Zr-3%Sn-1%Mo-1%Nb) in the temperature range of 350-550°C and a broad range of stress up to $\sim 750 \, \text{MPa}$ Pahutova et al. [42] reported a stress exponent of 3 and more than 20 at strain rates of about $1 \times 10^{-9} \, \text{s}^{-1}$ and $1 \times 10^{-5} \, \text{s}^{-1}$, respectively. The apparent activation energy for creep, $Q$, was found to be strongly dependent on temperature and slightly on stress. Other studies by Pahutova et al. [43] [44] on Zr-Mo alloys and Zr-6%Sn-1%Mo alloy showed similar values of stress exponent and similar trends, i.e. stress exponent lower than 4 and higher than 14 for low strain rates ($< 1 \times 10^{-6} \, \text{h}^{-1}$) and high strain rates ($> 3 \times 10^{-5} \, \text{h}^{-1}$), respectively.

In a literature review of creep data for Zr, Hayes and Kassner [45] presented the available data in a plot of diffusion coefficient compensated steady state creep rate versus shear modulus compensated stress (Figure 2-8). In the low stress region the stress exponent is about 1.1 which corresponds to Harper-Dorn creep. At intermediate stress levels the stress exponent is equal to $\sim 6.4$ which can be considered as the power-law creep region and finally at high stress levels there is the power-law breakdown region.
Figure 2-8 Diffusion coefficient-compensated steady-state strain rate vs. modulus-compensated steady-state stress data for zirconium [45]

Bell [46] investigated the effect of different heat treatments on the thermal creep properties of Zr-2.5Nb pressure tube at 450°C. It was found that water-quenching from solution treatment temperatures of 650-850°C and aging at 500°C for 24 hours results in anisotropic creep behaviour while water-quenching from temperatures higher than 850°C (approximately the $\alpha_{Zr} + \beta_{Zr} \rightarrow \beta_{Zr}$ transformation temperature) results in isotropic creep properties. The creep of air-cooled samples was found to be anisotropic for all solution treatment temperatures. A 100 times reduction in the creep rate in the transverse direction
of the sample air-cooled from 880°C compared to the cold-worked pressure tube is reported. Air-cooled axial samples showed better creep resistance than cold-worked material, however not as much as in the transverse direction (creep rate about 10 times lower at 450°C and <207MPa).

Li and Holt [47] studied the effect of texture on the anisotropy of thermal creep of internally pressurized Zr-2.5Nb micro-pressure tubes in the temperature range of 300-400°C. It was found that creep anisotropy (ratio of axial to transverse steady-state creep rate, $\varepsilon_a / \varepsilon_t$) increases as the difference between resolved volume fraction of basal poles in the transverse and radial directions ($f_t - f_r$) increases. The tubes with the strong radial texture component (fuel sheathing texture) exhibited negative axial creep strain and negative creep anisotropy ratio ($\dot{\varepsilon}_a / \dot{\varepsilon}_t$) while tubes with strong transverse texture (pressure tube texture) showed positive creep anisotropy ratio and good creep resistance in the transverse direction. They reported a stress exponent of 3 and 6.4 for transverse stresses of 100-250 MPa and 250-325 MPa, respectively.

2.4 In-Reactor Deformation

Due to the strong texture of pressure tubes as well as the inherent anisotropy of the $\alpha_{Zr}$ hexagonal crystal structure, the in-reactor deformation is anisotropic. There are three main components to the in-reactor deformation of pressure tubes namely, irradiation growth, irradiation creep, and thermal creep. Thermal creep was discussed in the previous section. In this section the irradiation growth and the irradiation creep phenomena will be discussed.
2.4.1 Irradiation Growth

Irradiation growth is the shape change without significant volume change due to fast neutron fluence in the absence of applied stress. Irradiation growth was first observed and theorized in zirconium by Buckley who proposed condensation of interstitials as dislocation loops on prismatic planes and condensation of vacancies as loops on basal planes. However this mechanism does not explain the faster growth in polycrystalline zirconium, first observed by Kelly and later by other researchers, in which no evidence of c-component loops were found at low fluences (1×10^{25} n.m^{-2}) [48]. Carpenter et al. [49] studied the irradiation growth of Zr single crystals in the temperature range of 80°C - 280°C at fluences up to 2×10^{25} n.m^{-2}. An expansion along the a axis and a contraction along the c axis (strain of about 10^{-4}) was observed. The axial expansion of Zr was attributed to absorption of interstitials to a-type dislocations and interstitial loops. The irradiation growth was observed to saturate at fluences less than 5×10^{24} n.m^{-2}. In another study by Rogerson and Zee [50] it was found the growth saturation in zirconium single crystal is a temporary transient phenomenon and growth continues to fluences as high as 7×10^{25} n.m^{-2}. Furthermore, Zee et al. [51] found that heavily deformed Zr single crystals show high growth rate at 80°C that continues in a steady-state manner without saturation to high fluences. The proposed mechanism for this behaviour is annihilation of interstitials at a-type dislocations together with absorption of vacancies to c-component dislocations and oriented twin boundaries. Also it was found that the growth rate of heavily deformed single crystals increases with dislocation density which is qualitatively in agreement with polycrystalline material behaviour.

The generally approved mechanism for irradiation growth in zirconium alloys is Diffusional Anisotropy Difference (DAD) between the vacancies and interstitials which
was proposed by Woo [52]. In this mechanism it is proposed that vacancies and self-interstitials exhibit anisotropic diffusion in Zr due to its hcp crystal structure, and further the diffusional anisotropies of vacancies and self-interstitials are different. This causes segregation of defects into sinks with different orientations. If the strain direction of a sink correlates with its orientation, irradiation growth occurs. For boundaries it is obvious that the strain direction is normal to the boundary. In the case of dislocation loops the plane of a-type loops and some parts of the dislocation line direction are normal to the basal plane. For c-component loops both the loop plane and dislocation line direction are lying on the basal plane. In a coarse grain material where the dislocation sinks are dominant, preferential absorption of self-interstitials to the c-component loops and vacancies to the a-type loops results in the shrinkage in the c direction and expansion in the a direction, a behaviour that is observed experimentally [2].

In an investigation of point defect mobilities in zirconium Griffiths et al. [53] studied the effect of high voltage electron irradiation at 230-300K on a Zr sample pre-irradiated with neutrons at 740K. The pre-existing cavities in the foil due to neutron irradiation or new cavities induced by electron irradiation were observed to grow along the c axis and shrink along the a axis suggesting the existence of a Diffusional Anisotropy Difference (DAD) between interstitials and vacancies in αZr.

The amount of cold work is known to have an effect on irradiation growth of polycrystalline Zr alloys [54]. Figure 2-9 shows graphs of the growth strain versus neutron flux for Zircaloy-2 at annealed and 25% cold worked conditions at 353 K and 535 K. As can be seen, at low temperatures the growth strain is very significant for the
cold worked condition. However at higher temperatures (673K) the difference between cold-worked and annealed Zircaloy-2 is less pronounced [54].

Figure 2-9 Effect of cold work and temperature on irradiation growth of Zircaloy-2 [54]

Holt et al. [55] studied the effect of crystallographic texture on the irradiation growth of polycrystalline Zr-2.5Nb alloy. Micro-Pressure Tubes (MPT) with typical crystallographic texture of pressure tubes, i.e. strong transverse component in basal pole figure, and fuel sheathing with strong radial component in basal pole figure were irradiated up to fluences of $1.7 \times 10^{26}$ n.m$^{-2}$ (Figure 2-10). For both textures the resolved volume fraction of basal poles in the axial direction is very low (0.09 for MPT and 0.07 for fuel sheathing). The results show that both of the textures exhibit elongation in the axial direction and shrinkage in the transverse direction of the tube; however the fuel
sheathing with strong radial texture exhibits higher shrinkage in the transverse direction while the axial expansions are comparable.

![Figure 2-10 Axial and transverse growth strains for unstressed capsules irradiated in Osiris at nominal temperatures of 553 K and 583 K [55]](image)

### 2.4.2 Irradiation Creep

Irradiation and thermal creep processes are shape changes at constant volume under an applied stress at high temperatures with and without fast neutron fluence respectively [2]. In the current operating conditions of CANDU reactors the contribution to the total deformation of thermal creep (~10%) is small compared to irradiation creep (~70%), however it becomes more important at higher stresses and temperatures [47] for example in the design of Generation IV CANDU reactors. Regarding the effect of temperature on the creep rate, Figure 2-11 shows the semi-log plot of creep rate versus inverse temperature for different zirconium alloys. The general trend is that at low temperatures, irradiation creep is predominant while in the intermediate to high temperature range, thermal creep becomes the major component.
Irradiation can alter the creep behaviour of, either by hardening the material and decreasing the creep rate or by activating and/or enhancing deformation processes causing acceleration in creep [56]. The former case, i.e. thermal creep retardation due to hardening is a transient phenomenon noticeable mainly in annealed materials near or above yield stress.

2.4.2.1 Irradiation Creep Mechanisms

In this section some of the irradiation creep mechanisms are introduced. This section is mostly based on the work by Franklin et al. [57] and Was [58]; however more detailed information and mathematical representation of the models can be found elsewhere [59][60][61].
Irradiation Induced Creep

Irradiation induced creep refers to those mechanisms in which creep is only due to neutron flux. The total in-reactor creep rate would be a superposition of thermal creep and irradiation-induced creep. There are three hypotheses for the irradiation-induced creep mechanism which are discussed briefly in the following sections. Two common features of these mechanisms are the formation of dislocation loops due to irradiation and net transfer of atoms from planes of one orientation to another.

Stress-Induced Preferred Nucleation (SIPN) of Dislocation Loops

In this mechanism creep occurs due to the mass transfer by formation of dislocation loops from irradiation-induced self-interstitials. These interstitial loops nucleate preferentially between atomic planes perpendicular to an applied tensile stress. This mass transfer by preferred nucleation of self-interstitial loops may be accompanied by preferred nucleation of vacancy loops parallel to the tensile stress. Therefore, the material elongates in the direction of tensile stress as shown schematically in Figure 2-12 [57].

Figure 2-12 Schematic illustration of SIPN mechanism [57]
In a review by Matthews and Finnis [59] it is argued that while observations are in support of preferred loop orientation due to tensile stress, the magnitude of observed creep strains are 2-4 times higher than the predictions of SIPN. The greatest limitation of this model is that based on this model once the loops are nucleated the strain rate should be independent of stress and the creep should continue even if the stress is removed which is contrary to the observed behaviour.

**Stress-Induced Preferred Absorption (SIPA)**
This mechanism is similar to SIPN in the sense that it is stress-induced and involves dislocation loops. However, in this case it is the growth rather than the nucleation of dislocation loops which is biased by the applied tensile stress. In this mechanism, self-interstitials are preferentially absorbed at dislocation loops oriented perpendicular to the tensile stress. The possible origins of SIPA are the elastic interaction between the stress field of the defect and that of the dislocation or anisotropic diffusion [58].

**Yielding creep (Internal Stress Driven Creep)**
When there is no external stress on a polycrystalline material, individual grains deform only due to irradiation growth. However, in a polycrystalline material, each grain is constrained by the surrounding grains and it can not deform freely. As a result, internal stresses build up among grains which can be relieved by plastic yielding or creep. The effect of applied external stress is to bias this plastic deformation in the direction of the applied stress. Since this mechanism is triggered by irradiation growth, it exhibits a weak temperature dependence. In this model the irradiation creep is found to be very sensitive to the thermal creep stress sensitivity [59].
Irradiation Enhanced Creep

Irradiation-enhanced creep, which is referred to as those mechanisms in which irradiation enhances the rate of operative thermal creep mechanism. It can be subdivided into four mechanisms: 1) mobile dislocation production, 2) solute trapping, 3) jog dragging, and 4) climb-glide. These are discussed below.

Mobile Dislocation Production

In this mechanism, the creep rate is increased as a result of an increase in the number of dislocations due to radiation damage. It may be considered significant in a situation where creep rate is controlled by the number of dislocations being able to surmount the obstacles and glide [57].

Solute Trapping

Solute atoms are believed to act as creep retardants through interaction with dislocations. Therefore, trapping of solute atoms at irradiation-induced defects would result in an increase in the creep rate [57].

Jog Dragging

Creep rate in this mechanism is controlled by the rate of movement of jogs on screw dislocations. Screw dislocations can move freely on several slip planes by the cross-slip mechanism. However, jogs on screw dislocations are edge components and can only move by a climb mechanism which involves absorption or emission of self-interstitials and vacancies (Figure 2-13). It is proposed that preferred absorption of irradiation-induced self-interstitials at these jogs enhances their motion [57].
Climb-Glide
Similar to jog dragging mechanism, edge dislocation climb is enhanced by absorption of irradiation-induced self-interstitials and vacancies. It is assumed that deformation is produced by glide of edge dislocations after overcoming obstacles by climbing. It is similar to the dislocation creep mechanism in thermal creep in a sense that the creep rate is controlled by the climb process while the glide process produces the creep deformation [57][58].

2.4.2.3 Effect of Texture on Irradiation Creep
In a study on Zr-2.5Nb pressure tube material at 570 K Coleman et al. [62] found that the irradiation creep rate in the axial direction is about twice that of the transverse direction (Figure 2-14), a behaviour which was attributed to the crystallographic texture to a large extent and to a lesser extent to the deformation substructure, i.e. preferred orientation of dislocations.
Figure 2-14 Effect of cold-work after extrusion on creep rate from stress relaxation tests; Material 1: cold-worked pressure tube; Material 3: heat treated pressure tube; Material 5: cold-worked small tube; Material 6: heat treated small tube [62]

Ibrahim [63] studied the in-reactor creep ductility of internally pressurized micro pressure tubes of cold-worked Zr-2.5 Nb and Zircaloy-2 at high stresses (transverse stresses of up to 495 MPa and up to 13.8% and 18.1% transverse strain for Zr-2.5%Nb and Zircaloy-2 respectively) and a temperature of 571 K and an average fast neutron flux of $2.2 \times 10^{17}$ n.m$^{-2}$s$^{-1}$. The results showed that all the tubes exhibit a negative axial strain and positive transverse strain.

Holt and Ibrahim [64] proposed a model which relates the irradiation creep and growth of zirconium alloys to crystallographic texture. In their model the creep strain and growth strain are assumed to be additive and grains in each orientation are assumed to behave as
independent single crystals. The creep anisotropy can be related to the texture through the resolved volume fraction of basal pole normals in each direction, i.e. $f_a$, $f_r$, and $f_t$. They calculated the creep anisotropy of Zr-2.5Nb and Zircaloy-2 pressure tubes based on two categories of irradiation creep models: those in which dislocation climb is the strain producing mechanism and those in which glide is the strain producing mechanism. The model over-predicts the creep anisotropy ratio ($\frac{\varepsilon_a}{\varepsilon_i}$) for Zr-2.5Nb and Zircaloy-2 pressure tube for both climb and prismatic slip modes and greatly underestimates for basal slip mode. Good agreement with the experimental results was observed if the total strain is calculated based on 20% basal slip and 80% prismatic slip.

Causey [65] studied the irradiation creep anisotropy of Zr-2.5Nb and Zircaloy-2 alloys at 570 K and 320 K using stress relaxation in bending tests to eliminate the effect of irradiation growth. The creep anisotropy, i.e. the ratio of axial creep rate to the transverse creep rate ($\frac{\dot{\varepsilon}_a}{\dot{\varepsilon}_i}$), was found to be higher for Zr-2.5Nb than Zircaloy-2 at both temperatures and larger at 320 K than 570 K for both alloys. They used the model proposed by Holt and Ibrahim [64] to calculate the creep anisotropy based on crystallographic texture. At 570 K for both alloys 65% prismatic slip and 35% basal slip predicts the observed strains whereas at 320 K 84% prismatic and 16% basal slip in Zr-2.5Nb and 73% prismatic and 27% basal slip in Zircaloy-2 predicts the observed strains better. The higher creep anisotropy in Zr-2.5Nb is due to stronger texture compared to Zircaloy-2 material with equivalent fabrication route.

Holt et al. [55] studied the anisotropy of in-reactor deformation of Zr-2.5Nb pressure tubes and found that diametral strain rate increases and axial elongation rate decreases as the resolved fraction of basal plane normal increases in the radial direction and decreases
in the transverse direction and remains unchanged in the axial direction. Figure 2-10 shows the growth anisotropy in Micro-Pressure Tube (MPT) with similar texture as pressure tube, i.e. strong transverse component in the basal pole figure, and fuel sheathing with strong radial component in the basal pole figure. It shows that the growth strain is more negative in the transverse direction for the MPT with strong transverse texture. Furthermore, the MPT expands in the axial direction. Assuming that creep and growth are additive, the creep strain (Figure 2-15.c and d) can be obtained by subtracting the growth strain from total strain (Figure 2-15.a and b). Transverse creep strain is larger than the axial component (both positive) in the MPT, however it is less than transverse creep strain in the fuel sheathing with a strong radial texture. Noticeable in Figure 2-15.b is the very low total axial strain of fuel sheathing compared to MPT.
Creep anisotropy can be expressed in terms of Hill’s equation which is a generalization of von Mises criterion:

\[
\sigma_f = \left[ F(\sigma_y - \sigma_z)^2 + G(\sigma_z - \sigma_x)^2 + H(\sigma_x - \sigma_y)^2 + 2L\tau_{yx}^2 + 2M\tau_{zx}^2 + 2N\tau_{xy}^2 \right]^{0.5}
\]  \hspace{1cm} (9)

where \( \sigma_f \) is the effective stress, \( x, y, \) and \( z \) are mutually perpendicular axes of anisotropy of the material, for example axial, transverse, and radial direction of a tube. \( F, G, H, L, M, \) and \( N \) are anisotropy parameters. If the axes of anisotropy are coincident with the principle stresses as in the case of internally pressurized tubes, and shear stresses are zero, equation (9) reduces to [66]:

\[
\sigma_f = \left[ F(\sigma_x - \sigma_y)^2 + G(\sigma_y - \sigma_z)^2 + H(\sigma_z - \sigma_x)^2 \right]^{0.5}
\]  \hspace{1cm} (10)
and $F+G+H=1.5$ by definition.

It can be shown that the principle creep rates $\dot{\varepsilon}_a$, $\dot{\varepsilon}_i$ and $\dot{\varepsilon}_r$ are given by:

$$
\dot{\varepsilon}_a = \frac{\dot{\varepsilon}_f}{\sigma_f} [F(\sigma_a - \sigma_i) - H(\sigma_r - \sigma_a)]
$$

$$
\dot{\varepsilon}_i = \frac{\dot{\varepsilon}_f}{\sigma_f} [G(\sigma_i - \sigma_r) - F(\sigma_a - \sigma_i)]
$$

$$
\dot{\varepsilon}_r = \frac{\dot{\varepsilon}_f}{\sigma_f} [H(\sigma_r - \sigma_a) - G(\sigma_i - \sigma_r)]
$$

(11)

Assuming a power-law creep equation,

$$
\dot{\varepsilon}_f = B \sigma_f^n
$$

(12)

where $B$ is a constant and $n$ is the stress exponent, the principle creep rates for the case of thin walled pressure tube with $\sigma_a = \sigma_i / 2$ and $\sigma_r = 0$ can be written as:

$$
\dot{\varepsilon}_a = B \sigma_f^{n-1} (0.5H - 0.5F)\sigma_i
$$

$$
\dot{\varepsilon}_i = B \sigma_f^{n-1} (G + 0.5F)\sigma_i
$$

(13)

$$
\dot{\varepsilon}_r = B \sigma_f^{n-1} (-G - 0.5H)\sigma_i
$$

Therefore, knowing two sets of steady state creep rate ratios, one can find the anisotropy parameters and correlate uniaxial creep data to the biaxial situation in the pressure tube. Also it can be seen that for isotropic materials $F=G=H=0.5$ under a pressurized thin wall tube stress state the axial creep rate, $\dot{\varepsilon}_a$, diminishes to zero.

### 2.4.2.4 Effect of Dislocation Density on Irradiation Creep

Regarding the effect of cold work, it has been shown that the creep rate is weakly dependent on dislocation density and increases with dislocation density (Figure 2-16); this dependence is more pronounced at low temperatures [56][67].
2.5 Texture Randomization

In zirconium alloys, the Burgers orientation relationship, a crystallographic orientation relationship between α-hcp and β-bcc phases when the alloy undergoes a phase transformation, states that \{0002\} planes in the α phase are parallel with the \{110\} planes in the β phase and also \langle 11\bar{2}0 \rangle \ direction in the α phase are parallel to \langle 111 \rangle \ directions in the β phase (Figure 2-17) [69].
Due to symmetry of the crystal structure of $\alpha$ and $\beta$ phases there are six equivalent orientation variants during the $\alpha \rightarrow \beta$ phase transformation and twelve equivalent variants upon the $\beta \rightarrow \alpha$ phase transformation (Figure 2-18) [70]. If all of the variants have the same probability of occurrence, i.e. no variant selection, or there is weak variant selection, then the final texture would be significantly randomized by an $\alpha \rightarrow \beta \rightarrow \alpha$ phase transformation process [71].
For isotropic materials with random texture the axial in-reactor creep is expected to be zero [72] as discussed in section 2.4.2.3 where it was shown that for a random texture with the Hill anisotropy parameters of $F=G=H=0.5$ the axial creep strain rate is zero. Therefore heat treatments or fabrication routes that result in less pronounced crystallographic texture will yield less dimensional changes.

Ibrahim and Holt [73] calculated the proportions of irradiation creep and growth of Zr-2.5Nb and Zircaloy-2 pressure tubes based on the irradiation creep and growth anisotropy calculated from crystallographic texture and observed axial and transverse strain rates. Among the studied pressure tubes they reported the estimated axial and transverse strain rates as well as the calculated creep and growth rates for a heat treated Zr-2.5Nb pressure tube (water-quenched from 1150 K close to the $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ transus; 10-15% cold drawn; annealed at 775 K for 24 hr) the basal pole figure of which is given in Figure 2-19.
It can be seen that the texture is more random compared to the typical pressure tube texture and the basal poles are almost evenly distributed in the axial, transverse and radial directions. The calculated Hill’s anisotropy parameters for this texture for the axial creep rate are $F=0.674$ and $H=0.799$ ($H-F=0.125$). Comparing these values with the anisotropy parameters for a cold-drawn Zr-2.5Nb pressure tube with strong transverse component in the basal pole figure, $F=0.737$ and $H=1.072$ ($H-F=0.335$); one expects lower axial creep rates for the pressure tube with more randomized texture.

The estimated transverse strain rate for texture in Figure 2-19 is slightly lower than the typical pressure tube texture ($12\times10^{-4}$ vs. $13.5\times10^{-4}$) whereas the axial strain is an order of magnitude lower ($1.7\times10^{-4}$ vs. $12.7\times10^{-4}$). The calculated creep rates per $10^{25}$ n.m$^{-2}$ for
the heat treated texture and typical pressure tube texture in the transverse and axial
directions are $\varepsilon_t = 17.5 \times 10^{-4}$, $\varepsilon_a = 1.3 \times 10^{-4}$ and $\varepsilon_t = 12.7 \times 10^{-4}$, $\varepsilon_a = 3.4 \times 10^{-4}$ respectively.
The calculated growth rates ($10^{25}$ n.m$^{-2}$) for these two textures in the transverse and axial
directions are $\varepsilon_t = -0.5 \times 10^{-4}$, $\varepsilon_a = 0.9 \times 10^{-4}$ and $\varepsilon_t = 0.8 \times 10^{-4}$, $\varepsilon_a = 9.3 \times 10^{-4}$ respectively.

2.6 Development of High-strength Creep-resistance Zr alloys
Research on the development of a creep resistant Zr alloy that can work at temperatures
as high as 450°C was started in the late 60s and early 70s. It was found that alloys with
compositions in the range 3-4%Sn, 0.5-1.5% Mo, and 0.5-1.5% Nb are promising
materials with high strength and high creep-resistance.
Williams et al. [74] studied thirteen Zr alloys with Sn, Mo, and Nb as the major alloying
elements. Sn is an $\alpha$-stabilizer with solid solution strengthening effect. Mo and Nb are $\beta$-
stabilizer elements that have the potential of precipitation hardening especially Mo which
precipitates as an intermetallic (ZrMo$_2$) in the binary Zr-Mo system. According to
Williams et al., the alloy CX (Zr-3.2%Sn-1.1%Mo-1.1%Nb), similar in composition to
Excel, had the best short term mechanical properties in the precipitation hardened
condition among other investigated alloys. Furthermore, they found that the change in
tensile properties of CX due to irradiation at 300°C is less than Zr-2.5Nb. Very little
change in tensile properties of CX in the aged condition was observed as a result of
irradiation ($4.8 \times 10^{19} - 2 \times 10^{20}$ n.cm$^{-2}$)$^2$ at 450°C. Therefore, it is expected to see very
little irradiation hardening or ductility loss in CX.

---

2 Typical fluence that a pressure tube encounters during its lifetime is about $10^{21}$ n.cm$^{-2}$.  

40
Ibrahim et al. [75] studied the creep-rupture properties of some Zr alloys studied by Williams et al. [74] including CX. They found that quenched and aged microstructures with highest short term strength exhibit highest creep-rupture strength at high stress levels and short times, however the rupture life is less sensitive to stress, i.e. steeper lines on the stress vs. rupture time plot, compared to air-cooled or hot-worked microstructures. According to the results of Ibrahim et al., among the investigated alloys CX showed the best creep-rupture properties. At high stresses (>294 MPa) and a temperature of 300°C the CX alloy has the best creep properties in the quenched and aged condition with a martensitic microstructure and fine precipitates. However, at lower stresses and higher temperatures it has the best creep properties when it is air-cooled from high in the \( \alpha + \beta \) region, to produce a fine Widmanstätten \( \alpha \) microstructure surrounded by a continuous network of \( \beta \)-phase. Breaking this continuous network of \( \beta \)-phase results in poorer creep-resistance.

Early studies on Excel (Zr-3.5%Sn-0.8%Mo-0.8%Nb) have shown that in the as-extruded and stress relieved condition, with a texture with slightly higher volume fraction of the basal pole normals in the transverse direction, the alloy has similar tensile strength to 27% cold-worked Zr-2.5Nb and its transverse creep rate is about one third that of Zr-2.5Nb in the similar as-extruded condition. Furthermore, in the cold-drawn condition (up to 15%) Excel still exhibits lower in-reactor creep rates compared to 27% cold-drawn Zr-2.5%Nb while at the same time having higher tensile strength. In terms of irradiation growth, early studies at 570 K and fluences of up to \( 1.25 \times 10^{25} \text{ n.m}^{-2} \) show that 8% cold-drawn and stress relieved Excel pressure tube is predicted to have 30% less irradiation growth in the long term compared to Zr-2.5Nb. In general, Excel has higher tensile
strength and lower in-reactor creep than Zr-2.5Nb in the same metallurgical condition which is advantageous especially to applications at higher temperatures and pressures [3]. Producing pressure tubes with low dislocation density and more equiaxed $\alpha$-grains is beneficial to in-reactor creep properties and therefore dimensional stability; however it reduces the tensile strength. Therefore, Excel alloy pressure tubes can be made with lower dislocation density and similar tensile strength to Zr-2.5Nb. These Excel alloy pressure tubes would then have superior in-reactor properties.

Early comparative studies on in-reactor creep rates [11] show that Excel has lower creep rates in comparison to Zr-2.5Nb by 21%, 41%, and 24% in the 5% cold-worked, 25% cold-worked and water-quenched, 10% cold-worked and aged conditions respectively. Tensile strength of 3-5% cold worked Excel pressure tubes is shown to be considerably higher than 30% cold-worked Zr-2.5Nb pressure tubes (up to 155 MPa higher UTS at room temperature). In the annealed condition the tensile strength of Excel pressure tubes are similar to 30% cold-worked Zr-2.5Nb pressure tubes.

The results of in-reactor tests show that in all metallurgical conditions, especially annealed tubes, Excel is expected to have much better dimensional stability in the long term as compared to Zr-2.5Nb [11].

Hydrogen uptake and delayed hydride cracking (DHC) is one of the life limiting factors in CANDU reactor pressure tubes. Cheadle et al. [11] compared the hydrogen uptake of Zr-2.5Nb in the cold-worked condition and Excel in the 5% cold-worked condition. They concluded quite similar hydrogen absorption behaviour in the two alloys. Khatamian et al. [76] and Ells et al. [77] reported higher hydrogen solubility limits in Excel compared to Zircaloy-2 and Zr-2.5Nb. Also Ells et al. reported almost indistinguishable stress
intensity factors for delayed hydride crack initiation, $K_{IH}$, in Excel and Zr-2.5Nb. However the delayed hydride cracking velocity (DHCV) is higher in Excel compared to Zr-2.5Nb; this limits the usefulness of Excel in existing CANDU reactor designs.

2.7 Generation IV CANDU-SCWR

Excel alloy (Zr-3.5%Sn-0.8%Nb-0.8%Mo) is a promising candidate material for pressure tube for Generation-IV CANDU® Super Critical Water-cooled Reactor (SCWR) design. Similar to current CANDU® reactors, the SCWR design is based on a heavy water moderator and individual pressure boundaries, which contain fuel bundles and coolant. However, the difference between SCWR and current design is that the coolant is light water with a pressure of 25 MPa and inlet and outlet temperatures of 350°C and up to 625°C, respectively. There are two main conceptual fuel channel designs: 1) High Efficiency Channel (HEC) 2) Re-Entrant Channel (REC).

In the HEC design, the calandria tube is eliminated and the pressure tube is in direct contact with the moderator with a temperature of about 80°C and is thermally insulated from the hot coolant (Figure 2-20.a). In the REC design, however, the pressure tube and the concentric inner tube are separated from the heavy water moderator by a calandria tube. The Super Critical Water (SCW) coolant flows between pressure tube and inner tube and at the end of the channel it turns and flows through the inner tube which contains fuel bundles (Figure 2-20.b). Operating temperature of the pressure tube is designed to be 350 to 400°C [12][13].
Because of different design and operating conditions, different requirements must be met for HEC and REC designs. In HEC, since the calandria tube is eliminated, the pressure tube plays the role of calandria tube as well and therefore it must meet its requirements, i.e. minimum possible elongation due to irradiation growth and irradiation creep. Since the operating temperature of HEC design is low, most of the deformation is expected to be irradiation driven. However, the REC design is more similar to the current pressure tube design and therefore it can accommodate axial elongation and the only problem to be considered is diametral expansion. Since the operating temperature of REC design is relatively high (400°C), thermal creep becomes an important issue together with irradiation creep and irradiation growth.

2.8 Experimental Techniques

2.8.1 Differential Scanning Calorimetry (DSC)
Differential scanning calorimetry (DSC) is one of the most widely used thermal analysis techniques. The basic principle behind this technique is quite simple; detecting thermal
changes in the sample by comparing it to a known reference while both are subjected to heating or cooling thermal cycles. There are two main variations of DSC namely, power compensation DSC and heat flux DSC, which is used in the present study. They differ in the initial signal that is used for thermal analysis. In power compensation DSC the sample and the reference are subjected to heating or cooling programs through separate, identical heat sources while the temperature of the sample and the reference is kept the same. The difference in the power input to the two heat sources required to keep the sample and reference temperature constant is then used as the output signal. However, in heat flux DSC both the sample and the reference are subjected to the same heating or cooling program through a single heat source and the difference in temperatures is used as the primary output signal. Figure 2-21 shows a schematic diagram of the power compensation and heat flux DSC [78][79].

The reference is either an inert material put in an identical crucible as the sample’s or it is the empty crucible itself. The DSC data is usually presented as thermal analysis curves, output signal (heat flow) as a function of temperature. Figure 2-22 shows a schematic illustrating the principles of differential thermal systems.
Figure 2-21 Schematic drawing of power compensation (top) and heat flux (bottom) DSC [79]

Figure 2-22 Schematic illustrating principles of differential thermal systems. For definition of the symbols see the text [80]
In Figure 2-22 $T_h$ is the temperature of the heat source, $T_{sm}$ is the temperature at the point where temperature is monitored on the sample, $T_s$ is the actual temperature of the sample, $C_{sm}$ is the heat capacity of the temperature monitoring station on the sample side, $C_s$ is the heat capacity of the sample and its crucible, $R_s$ is the thermal resistance between the heater (at $T_h$) and the temperature monitoring station on the sample side (at $T_{sm}$), $R_s'$ is the thermal resistance between the temperature monitoring station on the sample side (at $T_{sm}$) and the sample (at $T_s$), $dq_s/dt$ is the heat flow between $T_h$ and $T_{sm}$, $dq_{s}'/dt$ is the heat flow between $T_{sm}$, and $T_s$ and $T_{rm}$, $T_r$, $C_{rm}$, $C_r$, $R_r$, $R_r'$, $dq_r/dt$, and $dq_{r}'/dt$ are the same quantities for the reference.

For ideal systems it can be assumed that the sample side and reference side are thermally identical, i.e. $C_{rm} = C_{sm}$, $R_s = R_r \equiv R$, and $R_s' = R_r' \equiv R'$. Furthermore for the sake of analysis it is assumed that $C_s > C_r$ and the heat flow in the system is governed by Newton’s law:

$$dQ/dt = k\Delta T \quad (14)$$

where $dQ/dt$ is the heat flow between two points with a temperature difference of $\Delta T$ and a thermal conductivity of $k$ (inverse of thermal resistance $R$).

The heat flow to the sample side heats up the sample as well as the temperature monitoring station on the sample side.

$$dq_s/dt = C_{sm}dT_{sm}/dt + C_sdT_s/dt \quad (15)$$

Applying Newton’s law to equations (15) results in:

$$1/R(T_h-T_{sm}) = C_{sm}dT_{sm}/dt + C_sdT_s/dt \quad (16)$$

The same analysis can be applied to the reference side to obtain

$$1/R(T_h-T_{rm}) = C_{rm}dT_{rm}/dt + C_rdT_r/dt \quad (17)$$
The signal that is monitored in heat flux DSC is temperature difference \((T_{rm} - T_{sm})\) and the output heat flow signal is given by subtracting equation (17) from equation (16):

\[
T_{rm} - T_{sm} = RdT/dt(C_s - C_r) \quad (18)
\]

In equation (18), \(R\) is independent of the sample and reference and only is a function of the instrument [79][80].

There are many variables such as instrument specific variables as well as material related variables that might affect the DSC results. Sample preparation and contamination are variables that can be controlled to improve the output. Since the sample size is very small any contamination can have a significant impact on the results. Also heating chamber atmosphere must be selected based on the material under study. Another important variable is the heating and cooling rates which could affect the results depending on the nature of the reaction [79].

### 2.8.2 Energy Dispersive X-Ray Spectroscopy (EDS)

In this section the energy dispersive X-ray spectroscopy (EDS) technique is described mostly based on references [81][82]; however more detailed information can be found in [83][84][85][86].

The principles of energy dispersive X-ray spectroscopy (EDS) can be explained by the classical Bohr’s atomic model with electron-shell structure. There are several possible interactions between the electron beam and the material including emission of X-rays. There are two types of X-ray emission: 1) Bremsstrahlung and 2) characteristic. Bremsstrahlung occurs when the incident electron loses energy in the form of X-ray as a result of inelastic interaction with Coulomb forces of the atomic nucleus. This contributes
to the continuous background in the X-ray spectrum. Characteristic X-ray occurs when
the primary electron knocks out an inner-shell electron to a higher energy orbit, leaving
the atom with a vacancy in its inner shell in an excited state. When an electron from the
outer shells fills the inner shell vacancy the atom returns to its stable state and the energy
difference between the outer shell and vacant shell is released in the form of a
characteristic X-ray radiation. Therefore, the characteristic X-ray energy released
depends on the atomic number of the atom and the quantum energy levels (electron
shells) involved in the process. Figure 2-23 explains the naming and classification of
characteristic X-rays. For example if an electron is knocked out from K shell and another
electron from L shell fills the vacancy, the emitted characteristic X-Ray is called Kα
[82][87].

Figure 2-23 Classification of characteristic X-rays based on Bohr's model [87]
Quantitative EDS chemical analysis relies on the fact that the intensity of the characteristic X-ray peaks of each element in the material is proportional to its concentration:

$$\frac{C_i}{C_{(i)}} = K \frac{I_i}{I_{(i)}} \quad (19)$$

In the above equation $C_i$ is the concentration of element $i$ in the sample, $C_{(i)}$ is the concentration in a standard sample, $I_i$ and $I_{(i)}$ are corresponding measured intensities, and $K$ is the sensitivity factor which corrects for the difference between the generated and measured X-ray intensities due to the effects of atomic number ($Z$), absorption ($A$), and fluorescence ($F$). For thin TEM samples the absorption and fluorescence effects can be neglected. Cliff and Lorimer [81] showed that EDS quantitative analysis in TEM can be done without the need of a standard sample by using the ratio of the X-ray intensities of the elements in the sample:

$$\frac{C_A}{C_B} = K_{AB} \frac{I_A}{I_B} \quad (20)$$

where $k_{AB}$ is called the Cliff-Lorimer factor which is the same sensitivity factor but only takes into account the atomic number ($Z$) effect [81].

### 2.8.3 Diffraction

The basis of all kinematic diffraction phenomena whether by X-rays, neutrons, or electrons is Bragg’s law [88] which can be explained referring to Figure 2-24. In analogy to light optics when a monochromatic plane wave beam of wavelength $\lambda$ hits a plane of atoms at an angle $\theta$ it is reflected at an angle $\theta$. Bragg’s law states that in order for the reflected beams from adjacent parallel atomic planes to be in phase, the path difference
between the waves (ABC in Figure 2-24) must be an integral number of the wavelength of the incident beam, \( n\lambda \). With simple trigonometry, Bragg’s law can be derived and is as follows:

\[
2dsin \theta_B = n\lambda \quad (21)
\]

where \( d \) is the interplanar spacing of the atomic planes. If Bragg’s law is not satisfied, i.e. the incident angle is such that the reflected beams are out of phase, destructive interference happens and there will be either zero or weak reflection.

![Figure 2-24 Schematic illustrating the Bragg's Law [81]](image)

**2.8.3.1 Electron Diffraction**

To explain electron diffraction in TEM it is customary to simplify Bragg’s law by using vector notation. Figure 2-25 shows the wave vector (k-vector) diagram of the diffraction phenomenon.
In this illustration $\mathbf{k}_I$ and $\mathbf{k}_D$ are the incident and reflected wave vectors and $\mathbf{K}$ is the change in $\mathbf{k}$ due to diffraction as follows:

$$\mathbf{K} = \mathbf{k}_D - \mathbf{k}_I \quad (22)$$

In elastic electron scattering theory the electron beam is treated as a wave of amplitude $\psi_0$ and phase $2\pi kr$:

$$\psi = \psi_0 e^{2\pi kir} \quad (23)$$

where $k$ is the magnitude of the wave vector and $r$ is the distance the wave has propagated. By definition $k=1/\lambda$, and since only elastic scattering is considered here, then:

$$|k| = |k_0| = \frac{1}{\lambda} \quad (24)$$

Applying simple trigonometry to Figure 2-24 the following equation is obtained:

$$|\mathbf{K}| = \frac{2 \sin \theta}{\lambda} \quad (25)$$
If in Bragg’s law $n=1$, then it is easy to conclude that:

$$|K| = \frac{1}{d} \quad (26)$$

$K$ is defined as $g$ a reciprocal lattice vector, an important concept in electron diffraction. Therefore, by measuring the length of $g$ or the ratio of two reciprocal lattice vectors in an electron diffraction pattern, one can relate it to specific planes in the crystal lattice and index the diffraction pattern provided the wavelength of the electron beam is known.

In selected area diffraction (SAD) the diffracted beams coming from a small area of the sample are selected by an aperture. Therefore it is possible to infer the crystallography of the phase(s) by indexing the diffraction pattern originating from the selected area [81].

Convergent beam electron diffraction (CBED) is another TEM technique which gives local crystallographic information about the sample from areas as small as few nanometers by focusing the electron beam onto a small spot as opposed to parallel illumination in the selected area diffraction (SAD) technique. The symmetry of CBED pattern carries information about the crystal structure and space group of the diffracting volume [89]. This technique was employed in this study to investigate the crystal structure of precipitates in the Excel alloy. More details about selected area diffraction (SAD) and convergent beam electron diffraction (CBED) can be found in [90][91][92][93].

### 2.8.3.2 Macro-Texture-Neutron Diffraction

Due to fabrication processes such as extrusion, rolling, drawing, etc. grains in polycrystalline materials usually have a preferred orientation with respect to the external coordinate system, i.e. forming directions. The preferred orientation of grains in a
polycrystalline material is called crystallographic texture [94]. In materials science crystallographic texture is usually represented by pole figures. Figure 2-26 illustrates the principles of formation of pole figures. Crystallographic planes can be represented by their normals. The interception of a plane normal with an imaginary sphere of radius 1 which is centered on the crystal is called a pole (\{001\} poles in Figure 2-26.a).

In order to present the texture data in 2D, poles are projected onto the equatorial plane. In materials science most commonly stereographic projection (in Figure 2-26.b-c) is used which preserves the angular relationship between the crystallographic planes. The projection point is either the north or the south pole; the crystallographic poles are connected to the projection point and the intersection of the connecting line with the equatorial plane is the stereographic projection of that particular pole (Figure 2-26.b). Each pole on the pole figure can be characterized by two angles: \( \alpha \), the azimuth angle of the pole and \( \beta \), the polar angle (Figure 2-26.c) [94][95].
Figure 2-6.a shows the typical (0002) pole figure of extruded CANDU pressure tubes. It represents the distribution of basal plane normals with respect to the external coordinate system of the tube, i.e. axial, radial and transverse directions. The contours show the texture of the material in units of multiples of a random texture. It can be seen that most of the basal plane normals are oriented in the Radial-Transverse plane and biased towards the Transverse direction.
Another parameter that is frequently used in zirconium alloys to quantitatively describe the degree of anisotropy of the material is the resolved fraction of basal pole, $f$-parameter. It is defined with respect to a reference direction as:

$$f_d = \sum_{0}^{90} V_i \cos^2 \alpha$$  \hspace{1cm} (27)$$

where $f_d$ is the resolved volume fraction of basal poles in the $d$ direction (axial, radial, or transverse), $V_i$ is the volume fraction of grains having basal poles at an angle $\alpha$ to the $d$ direction [58][96].

$V_i$ can be calculated from the pole figure according to the following equation provided that the reference direction is in the centre of the pole figure:

$$V(\alpha, \beta) = \frac{TC(\alpha, \beta) \sin \alpha}{\sum \sin \alpha}$$  \hspace{1cm} (28)$$

where $\alpha$ and $\beta$ are azimuth and polar angles respectively and $TC(\alpha, \beta)$ is the texture coefficient at each certain $\alpha$ and $\beta$ which can be calculated from the relative intensities in the diffraction spectrum [64][97].

Bulk texture measurement with a neutron beam is based on the same principle of all diffraction phenomena, i.e. Bragg’s law. Neutron beam with a characteristic wavelength of 0.05-0.3 nm and a penetration depth of several centimetres is suitable for macro-texture measurement of bulk samples. Neutron texture measurement in this work was done at the National Research Universal (NRU) nuclear reactor located at the Chalk River Laboratories (CRL). A germanium crystal monochromator was used to select a single wavelength from broad spectrum thermal neutrons wavelengths. The detector and the incident beam are set at a fixed $2\theta_B$ angle corresponding to the Bragg angle of the particular set of crystallographic planes of interest. The sample is mounted on an Eulerian
cradle with radial direction of the pressure tube parallel to the \( \eta \) axis of the cradle (Figure 2-27). This configuration corresponds to the radial direction at the centre of the pole figure. The cradle rotates the sample along \( \eta \) and \( \chi \) at increments of 5° from 0° to 360° and 0° to 90° respectively so that the entire pole figure is covered. The detector can be programmed to rotate to different \( 2\theta_B \) angles to measure different sets of crystallographic planes.

![Figure 2-27 Eulerian Cradle and mounted sample showing rotation angles of \( \chi \) and \( \eta \)](image)

In this work neutron texture data analysis and pole figure construction were performed using MTEX [99] a free and open source software toolbox for MATLAB®.

### 2.8.3.3 Electron BackScatter Diffraction (EBSD)

Electron backscatter diffraction (EBSD) is a technique to measure the crystallographic orientation in a scanning electron microscope (SEM). The first electron backscatter pattern (EBSP) was reported by Nishikawa and Kikuchi [100] from a cleavage face of
calcite. First steps towards development of EBSD technique were taken by Venables and Harland [101] who installed an EBSD detector in a SEM. A computer aided EBSP indexing program was first introduced by Dingley capable of indexing cubic structures which was launched by Oxford Instruments [102]. Krieger-Lassen [103] was the first one to use the Hough transform for automatic detection of Kikuchi bands which is the basis of modern automated EBSP indexing.

In this technique a stationary electron beam hits the sample and the generated backscatter diffraction pattern is detected by a phosphorous screen. The depth at which the backscattered electrons originate inside the material is a function of atomic number and is in the order of a few tens of nm. Therefore, EBSD is a surface sensitive technique. Figure 2-28 shows a schematic describing the formation and geometry of electron backscatter patterns (EBSP). The point at which the primary beam impinges the sample is the centre of the pattern and the intersection of the two diffracting cones with the phosphorus screen forms a pair of almost straight Kikuchi lines; the centre of the Kikuchi band coincides with the projection of the diffracting crystallographic plane onto the phosphorus screen. EBSPs usually contain more than one Kikuchi band and the angle between Kikuchi lines corresponds to the angle between diffracting planes and the width of each Kikuchi band is twice the Bragg angle. Thus the width of the Kikuchi bands is related to the interplanar spacing of the diffracting planes through Bragg’s law.

Automatic acquisition and indexing of EBSPs is provided through the available commercial software which make EBSD a fast and unique tool for micro-texture measurement [104][105].
Figure 2-28 Principles and geometry of formation of electron backscatter Kikuchi patterns (EBSP) [105]
2.9 References


[98] W. Li, Effect of Texture on Anisotropic Thermal Creep of Pressurized Zr-2.5Nb Tubes, Queen’s University, 2009.
Chapter 3
Transformation Temperatures of Excel Alloy Pressure Tube Material

Abstract
The transformation temperatures of Zr alloy Excel (Zr- 3.5%Sn- 0.8%Nb- 0.8%Mo) pressure tube material were studied using metallography, differential scanning calorimetry (DSC) and resistivity measurement techniques. The $\alpha_{Zr} + \beta_{Zr} \rightarrow \beta_{Zr}$ transus temperatures obtained using these three methods are in good agreement with each other, 968, 962, and 975°C respectively. From the metallography and the DSC studies it was found that the volume fraction of stabilized $\beta_{Zr}$ starts to increase in the temperature range of 600-690°C. Furthermore, it was observed that the $\beta$-phase does not transform to $\alpha'$ martensite upon quenching from temperatures below about 860°C. It was first seen to fully transform to martensite after quenching from 864°C; a rapid increase in the volume fraction of $\beta$-phase occurs above this temperature.

3.1 Introduction
The thermal efficiency of CANDU reactors can be increased by increasing the coolant temperature, for example in the conceptual design of the Generation IV Super Critical Water CANDU reactor (CANDU-SCWR) a thermal efficiency of up to 40% can be achieved by increasing the coolant temperature from 300°C to 650°C in such a reactor by using a re-entrant channel design requiring the pressure tube to operate at 400°C [1][2].
This implies the need for a higher creep resistant material for the pressure tube than Zr-2.5Nb which is the current material in use. Excel alloy (Zr-3.5%Sn-0.8%Nb-0.8%Mo) is a good candidate material for pressure tubes. It is known that Zr-Sn-Nb-Mo alloys have higher strength and creep resistance compared to other Zr alloys [3][4] mainly due to the solid solution strengthening effect of Sn as well as the potential for age hardening in the $\alpha_{Zr} + \beta_{Zr}$ quenched condition. Williams et al. [5] showed that increasing the Sn content in ternary Zr-Sn-Mo has the effect of raising the strength and delaying overaging at 450°C and 500°C. Mo is a strong $\beta$-stabilizer with precipitation hardening potential, due to its very low solubility in $\alpha_{Zr}$. Nb has the same precipitation hardening effect as Mo but to a lesser extent at the same atomic percent, due to the higher solubility of Nb in $\alpha_{Zr}$. According to the study by Williams et al., the Zr-Sn-Mo-Nb alloys are precipitation hardenable only in the quenched condition from the $\alpha_{Zr} + \beta_{Zr}$ or $\beta_{Zr}$ region which results in very high strength and hardness but very low ductility (<6% total elongation). Air-cooling from the $\alpha_{Zr} + \beta_{Zr}$ region gives a microstructure consisting of equiaxed primary $\alpha_{Zr}$ grains and a fine Widmanstatten $\alpha_{Zr}$ (where prior $\beta_{Zr}$ existed at the heat treatment temperature) surrounded by a network of retained $\beta_{Zr}$-phase which has intermediate strength and ductility with no aging response [5]. According to Ibrahim et al. [4], who studied stress-rupture and creep properties of a variety of Zr-Sn-Mo-Nb alloys at 300-500°C and compared them with Zircaloy-2 and Zr-2.5 Nb, all of the Zr-Sn-Mo-Nb alloys in all metallurgical conditions exhibit much better stress-rupture properties than Zircaloy-2 or Zr-2.5Nb. Also they showed that CX (Zr-3.2%Sn-1.1%Nb-1.1%Mo) which is very similar to Excel, has much better creep
properties than Zircaloy-2 with the potential of being used above 400°C. Furthermore, Ibrahim et al. observed that the stress-rupture and high stress (>294 MPa) creep properties of CX alloy at 300°C are best in the quenched and aged condition, i.e. a microstructure consisting of martensite with precipitates, while at lower stresses and higher temperatures a Widmanstätten microstructure, which is obtained by air cooling, gives as good or better creep properties than a quenched and aged microstructure [4].

The first step in designing any heat treatment to improve the mechanical properties is to consult with the phase diagram in order to know the phase transformation temperatures and phase proportions. However, since there is no published phase diagram for the Zr-Sn-Nb-Mo quaternary system, this study aims to pinpoint the transformation temperatures as well as understand the evolution of potential microstructures to be obtained using different thermo-mechanical processing routes.

In this study, three different methods were employed to find the temperature at which the volume fraction of stabilized $\beta_{Zr}$ starts to increase and the $\alpha_{Zr} + \beta_{Zr} \rightarrow \beta_{Zr}$ transformation temperatures; 1) Heating and quenching from different temperatures followed by metallography and microscopy. 2) Differential Scanning Calorimetry (DSC), and 3) resistivity change measurement.

### 3.2 Material

The material used in this study is an Excel alloy pressure tube, a material consisting of $\alpha_{Zr}$-hcp and $\beta_{Zr}$-bcc phases, with the specified chemical composition given in Table 3-1. The tube was provided by AECL Chalk River Nuclear Laboratories and is designated XL 601. The tube was made by extruding a hollow billet preheated to 850°C at a ratio of 10:1.
followed by 25% cold drawing. The tube was then annealed at 750°C for 30 minutes and stress relieved at 400°C for 24 hours. Figure 3-1 shows the microstructure of the as received pressure tube.

Table 3-1: Chemical composition (wt.%) of the studied Zr-Excel alloy

<table>
<thead>
<tr>
<th></th>
<th>Sn</th>
<th>Mo</th>
<th>Nb</th>
<th>O</th>
<th>Fe</th>
<th>H*</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spec. Spec.</td>
<td>3.2-3.8</td>
<td>0.6-1</td>
<td>0.6-1</td>
<td>0.09-0.16</td>
<td>0.15</td>
<td>5 ppm (≤20ppm)</td>
<td>Balance</td>
</tr>
<tr>
<td>Measured</td>
<td>3.39-3.68</td>
<td>0.77-0.81</td>
<td>0.75-0.77</td>
<td>0.11</td>
<td>0.09-0.13</td>
<td>≤5 ppm</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Figure 3-1 TEM micrograph of the axial-radial cross section of the as-received Excel pressure tube

*The given H content is in the billet prior to extrusion; there might be up to 15 ppm H pickup during subsequent processing.*
3.3 Experimental Procedures

To find the transformation temperatures the following three methods were employed and compared: 1) quantitative metallography (heating and quenching), 2) differential scanning calorimetry (DSC) and 3) electrical resistivity. These techniques are described in more detail below.

3.3.1 Quantitative Metallography (Heating and Quenching)

Quenching from different temperatures followed by metallography and microscopy was used to study the transformation temperatures based on the microstructural changes. It is known that in β-stabilized Zr alloys, quenching from the $\alpha_{Zr} + \beta_{Zr}$ or $\beta_{Zr}$ region results in the transformation of $\beta_{Zr}$ to $\alpha'$–hcp martensite, $\alpha''$ orthorhombic martensite or $\omega$ hexagonal metastable phases, or a mixture of these depending on the solution treatment temperature and chemical composition of the alloy. The $\alpha'$–hcp martensite appears in two morphologies: lath (massive) martensite in dilute alloys and acicular martensite, while the $\omega$ phase is in the form of very fine (<0.5 nm) particles [6][7]. Therefore, the occurrence of any of these metastable phases in the microstructure of the heated and quenched sample suggests the presence of the $\beta$ phase prior to quenching.

For the heating and quenching experiment, samples with the approximate dimensions of 4.3x10x10 mm were cut from the pressure tube and the black oxide layer was ground off using P200 SiC paper. The samples were heated in a flushing argon (99.999 Ar, $O_2<1$ppm, $H_2O<3$ppm, $N_2<4$ppm, and THC<0.5ppm) environment inside a quartz tube in a LINDBERG/BLUE Mini-Mite™ tube furnace. In total 16 different temperatures for solution treatment were selected: 600, 690, 752, 763, 790, 800, 808, 826, 846, 864, 876,
895, 904, 916, 930 and 968°C. The temperature of the samples was measured by an Omega K-type Super OMEGACLAD® XL (an Inconel alloy) sheathed thermocouple inserted into a drilled hole in the samples. Each sample was held at its maximum temperature for two hours in order to allow the possible phase transformation to complete. Using the diffusion equation reported by Balluffi and Resnick which is obtained by a sandwich type diffusion couple of pure Zr and Zr-5wt% Sn [12], the diffusion distance of Sn in Zr after 2 hours at 600°C, which is in the lower temperature range in this experiment, can be calculated to be $6 \times 10^{-6}$ m as follows [13]:

$$D = \bar{D}_0 \exp\left(-\frac{Q}{RT}\right) \quad (1)$$

$$d = 2.4\sqrt{Dt} \quad (2)$$

where $\bar{D}_0 = 3.0 \times 10^{-6} \text{cm}^2\text{s}^{-1}$ is the chemical diffusion constant of Sn in Zr, $Q = 92 \text{kJ.mol}^{-1}$ is the activation energy [12], $R$ is the gas constant, $T$ is the absolute temperature, $d$ is the diffusion distance, and $t$ is time.

The same calculation for oxygen with the diffusion constant of $\bar{D}_0 = 1.32 \text{cm}^2\text{s}^{-1}$ and the activation energy of $Q = 201.8 \text{kJ.mol}^{-1}$ results in a diffusion distance of approximately $2 \times 10^{-6}$ m. There is no diffusion data for Mo, Nb, and Fe in or close to the temperature range of interest in the literature.

The diffusion distance of $6 \times 10^{-6}$ m and $2 \times 10^{-6}$ m for Sn and O is comparable to or larger than the grain size of the as-received material (Figure 3-1). Therefore given the solution treatment time, the alloy is close to the equilibrium condition.

For optical microscopy and scanning electron microscopy (SEM), samples were prepared by grinding to P1200 SiC paper followed by attack polishing using a solution of 5% HF,
5% HNO₃, 5% H₂O₂, and 85% distilled water mixed with 0.05 µm colloidal silica at an approximate ratio of 1:4. A JEOL JSM-840 instrument was used for scanning electron microscopy (SEM). The SEM micrographs were taken using the back-scattered mode at 20 kV accelerating voltage and 8mm working distance in order to give a good compositional contrast. The β-phase volume fraction measurements were performed using the manual point counting method according to the ASTM E562-11 standard. At least five areas of approximately 2500 µm² with about 1000 points for each sample were counted [15]. The samples for transmission electron microscopy (TEM) were cut to thin slices (200-300 µm) using an Accutom-5™ precision cut-off saw followed by hand grinding on P1200 SiC to 70-80 µm. Then the samples were thinned electro-chemically using a solution of 5.3 g LiCl, 11.16 g Mg(ClO₄)₂, 100 ml Butyl cellosolve, and 500 ml methanol at -45°C in a TenuPol-5™ twin-jet electropolisher. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) analysis were done using a Philips CM 20 TEM equipped with a Noran Vantage EDS detector. The working conditions for EDS analysis were 200 kV accelerating voltage and 75 nm beam size for all of the samples. The quantitative chemical analysis was performed using the Noran Vantage software and applying a Gaussian fit to the EDS spectrum. The quantitative EDS analyses were performed using a standard-less method.

3.3.2 Differential Scanning Calorimetry (DSC)
Differential scanning calorimetry (DSC) is a widely used method to determine phase transformation temperatures in many different materials. Toffolon-Masclet et al showed
that with the new high resolution state of the art instruments not only is it possible to study phase transformations but also very low energy phenomena such as precipitation [8].

The DSC technique is based on the fact that any microstructural change such as phase transformation or recrystallization that is either endothermic or exothermic can be detected by the change in the sample temperature compared to a reference, where both the sample and the reference are subjected to the same heating program. The measured signal is sample temperature, which lags behind the reference temperature in the case of an endothermic event and rises faster in the case of an exothermic event.

The DSC test was carried out on a 4x4x4 mm sample using a SETSYS™ DSC/TGA heat flux instrument in an argon atmosphere (99.999% purity) with a flow rate of 20 ml/min. The chamber was pumped and purged three times to ensure the least possible contamination with oxygen. The heating cycle was programmed to heat up and cool down the sample between 23-1000°C at a rate of 10°C/min with a 1 hour hold at 1000°C between heating and cooling. Al₂O₃ was used as the reference material.

### 3.3.3 Electrical Resistivity Measurement

Electrical resistivity of pure metals increases linearly with temperature according to the following equation [9]:

\[
\rho_T = \rho_r (1 + \alpha \Delta T) \tag{3}
\]

where \( \rho_T \) is the resistivity at any temperature, \( \rho_r \) is the resistivity at room temperature, \( \alpha \) is the temperature resistivity coefficient, and \( \Delta T \) is the temperature difference between room temperature and the temperature of interest.
For alloys, Matthiessen's rule states that the increase in resistivity due to addition of solute atoms is independent of temperature, i.e. the total resistivity at any temperature can be calculated as the sum of two terms: the intrinsic resistivity of the pure base metal, $\rho_i$, given by equation (3), and the temperature-independent residual resistivity due to solute atoms, $\rho_0$ [10]:

$$\rho_{\text{total}} = \rho_i + \rho_0$$  \hspace{1cm} (4)

However, it has to be pointed out that the temperature dependence of resistivity in Zr alloys deviates from the Matthiessen’s rule linear trend. In the case of $\beta_{Zr}$-stabilized Zr alloys, when the volume fraction of $\beta_{Zr}$ starts to increase at the lower transus temperature, the chemical composition of the $\alpha_{Zr}$ and $\beta_{Zr}$ phases starts to change as well. Therefore, the resistivity of the material deviates from its previous non-linear increasing trend and starts to decrease because of the lower resistivity of the $\beta_{Zr}$-phase. The resistivity keeps dropping upon heating until all the microstructure transforms to $\beta_{Zr}$, at which point it starts to increase again but at a different rate. In order to find these two deviation points, i.e. the transformation temperatures, in this study the approach used by Canay et al. [11] was employed in which a polynomial is fitted to the resistivity versus temperature curve and the point where the first derivative equals zero is taken as the transformation temperatures.

The same setup as in the heating and quenching experiment was used for resistivity measurement except that heating was continuous at constant rates of 20°C/min and 47°C/min. The sample dimension was approximately 4.3x10x10 mm cut from the pressure tube; again the black oxide layer was ground off using P200 SiC paper. Two Pt wire leads were spot welded to the top and bottom of the rectangular prism shape sample.
in order to apply a constant DC current of 2 A to the sample. Between the current leads on the sample’s face, two other Pt wire leads were spot welded to read the voltage across the sample. A KEPCO® ATE 25-10 DM power supply was used to apply the constant current and a KEITHLEY 2701 digital multi-meter was used to read the voltage across the sample with an accuracy of $\pm 0.5 \mu V$. Since the current is constant throughout the experiment, the resistance at each temperature is directly proportional to the voltage; hence any change in the voltage reading can be directly interpreted as a change in the resistivity of the material. It has to be mentioned that since the important parameter in this study was the change in resistivity rather than the absolute value of resistivity, the sample dimension is not of a great importance and any sample size could be used. For the same reason, the voltage reading at each temperature, $V$, was normalized by the initial voltage at room temperature, $V_0$, and then plotted versus temperature. Similar to the heating and quenching experiment an Omega K-type Super OMEGA CLAD® XL sheathed thermocouple, inserted into a drilled hole in the sample was used to record the temperature. However, since the maximum temperature was higher than the heating and quenching experiment and Zr forms a eutectic with Ni at 960°C [14], the tip of the thermocouple was wrapped in 99.8 wt% pure Nb foil in order to avoid the eutectic reaction. Pt wire leads were spot welded to the sample to apply a constant DC current of 2 A to the sample and to read the voltage across the sample.
3.4 Results

Figure 3-2 shows representative back-scattered SEM micrographs of the quenched samples as well as the as-received pressure tube material used for volume fraction measurement. Due to the Z-contrast, the bright phase in Figure 3-2.a-f is the $\beta_{Zr}$-phase which is rich in heavier elements, Mo and Nb. By increasing the solution treatment temperature the volume fraction of $\beta_{Zr}$ or transformed $\beta_{Zr}$ increases in Figure 3-2 a-e until at 968°C (Figure 3-2 f) the microstructure is fully transformed $\beta_{Zr}$, i.e. fully martensitic. The volume fraction of $\beta_{Zr}$-phase as a function of temperature is presented in Figure 3-3; the rapid increase in the $\beta_{Zr}$-phase volume fraction at 864°C corresponds to $\beta_{Zr}$ fully transformed to $\alpha'$ in Figure 3-2.d. Below 864°C, the $\beta_{Zr}$-phase does not fully transform to martensite (Figure 3-2c) and $\beta_{Zr}$ remains untransformed with only a few martensite laths inside the $\beta_{Zr}$ grains (indicated by arrows in Figure 3-2c).
Figure 3-2 Electron back-scattered SEM micrographs of a) as received, and water quenched samples after 2 hours solution treatment at b) 690 c) 846, d) 864, e) 930, f) 968°C. Note that at temperatures of 846°C and below, the β-phase is not completely transformed to martensite.
Figure 3-3 Volume fraction of beta-phase (%) as a function of temperature from which the samples were quenched. Error bars are determined according to the 95% confidence interval formula in ASTM E562-11 [15].
Figure 3-4 presents the transmission electron micrographs together with the energy dispersive X-ray spectroscopy (EDS) data from the samples quenched from 690, 846, and 876°C corresponding to completely retained, partially retained, and fully transformed $\beta$ respectively; the Cu and Pt peaks in the EDS spectra are from the sample holder. Figure 3-5 shows the concentration of Mo, Nb, and Fe in the $\beta$-phase as a function of temperature. At least four EDS spectra were collected for each sample and the standard deviation is reported as the error.

Figure 3-4 Top: TEM micrographs of samples quenched from a) 690 b) 846 and c) 876°C Bottom: Typical EDS spectra from 690°C sample d) $\alpha_{Zr}$-phase e) $\beta_{Zr}$-phase (Cu and Pt peaks are from the sample holder)
Figure 3-5 Concentration (wt.%) of Nb, Mo, and Fe in beta phase as a function of temperature from which the samples were quenched.

A TEM micrograph and selected area diffraction (SAD) pattern of the sample water-quenched from 800°C is shown in Figure 3-6. The area from which the SAD pattern was taken is marked by a circle. Also shown in Figure 3-6 is a schematic SAD pattern reconstructed by inputting the space group and lattice parameter data of $\beta$ and $\omega$ phases into the Web Electron Microscopy Applications Software (WebEMAPS) [16] an online tool for electron microscopy simulations.
Figure 3-6 TEM micrograph and selected area diffraction (SAD) pattern of the sample water-quenched from 800°C. The bottom right is the reconstruction of the $\beta$-phase and $\omega$-phase diffraction pattern.

The result of differential scanning calorimetry (DSC) at a heating and cooling rate of 10°C/min is presented as the heat flow vs. temperature graph in Figure 3-7. 10°C/min heating rate was chosen so that it is close to quasi-equilibrium conditions. Slower heating rates were not tried due to the higher chance of oxygen absorption, which affects the transformation temperatures.
Figure 3-7 DSC curve at a heating and cooling rate of 10°C/min

Shown in Figure 3-8 is the graph of normalized voltage ($V/V_0$) vs. temperature. The experiment was done at two different heating rates: 20°C/min and 47°C/min. The 47°C/min test was repeated on the same sample to see the effect of oxygen pickup. Since oxygen is an $\alpha_{Zr}$-stabilizer, it is expected to raise the transformation temperatures.

Figure 3-8 Normalized voltage ($V/V_0$) vs temperature at heating rates of 20°C/min and 47°C/min
3.5 Discussion

Heating and quenching experiments show that the volume fraction of β-phase remains constant at 13±0.5% up to 600°C; it increases to 19±2% at 690°C (Figure 3-2.a-b and Figure 3-3). Therefore, the $\alpha_{Zr} \rightarrow \alpha_{Zr} + \beta_{Zr}$ transformation temperature, i.e. the temperature at which the volume fraction of $\beta_{Zr}$-phase starts to increase, is in the range between 600°C and 690°C. However, the $\beta_{Zr}$-phase remains un-transformed after quenching from a temperature of up to 846°C with few martensite laths formed (Figure 3-2.c). Upon quenching from 864°C all of the $\beta_{Zr}$-phase has transformed into martensite (Figure 3-2.d). Repeating the 866°C sample resulted in the full transformation of the $\beta_{Zr}$-phase into martensite. This could be attributed to slight temperature differences between the two samples, within the accuracy of the temperature measurement, and suggests that 866°C is the threshold temperature below which transformation of the $\beta$-phase into martensite is hindered. The retention of the $\beta_{Zr}$-phase on quenching is discussed below. Finally at 968°C all of the microstructure consists of transformed $\beta_{Zr}$ (except one or two small isolated alpha particles) which indicates that 968°C is approximately the $\alpha_{Zr} + \beta_{Zr} \rightarrow \beta_{Zr}$ transformation temperature (Figure 3-2.f).

From the differential scanning calorimetry (DSC) experiment if the deviation point from linearity in Figure 3-7 (dotted lines) is taken as the onset of the transformation, the $\alpha_{Zr} \rightarrow \alpha_{Zr} + \beta_{Zr}$ and $\alpha_{Zr} + \beta_{Zr} \rightarrow \beta_{Zr}$ transus temperatures can be found to be 628°C and 962°C respectively for the heating cycle and 495°C and 990°C for the cooling cycle. Full baseline analysis in order to determine the transformation temperatures with more accuracy was not possible due to the fact that the test was interrupted at 1000°C and the plateau region after the peak was not quite established.
The considerably lower $\alpha_{Zr} \rightarrow \alpha_{Zr}+\beta_{Zr}$ temperature obtained during the cooling cycle could be explained by the undercooling required for the transformation to start. Also, the higher $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ temperature during cooling could be attributed to oxygen pickup upon heating.

Studying a phase transformation using the resistivity measurement technique is based on the fact that any phase transformation in the alloy changes the resistivity. In the case of the dual phase Excel alloy, up to the temperature at which the volume fraction of $\beta_{Zr}$ starts to increase, the alloy is expected to behave like other Zr alloys, i.e. deviation from Matthiessen’s rule especially at high temperatures. However, when the volume fraction of $\beta_{Zr}$ starts to increase there is a change in the relative amount of each phase as well as the composition of phases, therefore the resistivity deviates from its previous trend and starts to decrease because the resistivity of $\beta_{Zr}$ is lower than $\alpha_{Zr}$ [10]. This decrease in resistivity continues until all the microstructure is $\beta_{Zr}$ and the resistivity again starts to increase but with a different slope. Here we are looking for these two temperatures at which the alloy deviates from its previous trend.

Using the curve fitting approach and $\frac{dV}{dT} = 0$ criterion [11] in Figure 3-8 we obtain the $\alpha_{Zr} \rightarrow \alpha_{Zr}+\beta_{Zr}$ transformation temperature 745, 785, and 794°C for 47°C/min, 47°C/min repeated, and 20°C/min heating rates respectively. The higher transformation temperature in the last two heating cycles is most probably due to absorption of oxygen which is a strong $\alpha$-stabilizer.

The $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ transformation temperature is found to be 979, 975, and 975°C for the above mentioned heating rates, respectively, which thus seems to be constant irrespective of the heating rate.
Figure 3-9 shows the SEM micrographs of the samples with the 47°C/min heating rate and the repeated sample (Figure 3-8). It is clear that the layer of the remnant equiaxed alpha in the repeated sample, which is due to oxygen pickup, is wider than in the first sample. This is due to the fact that oxygen is an \( \alpha_{Zr} \) stabilizer; therefore the thicker layer of the equiaxed \( \alpha_{Zr} \) suggests a deeper diffusion distance of oxygen into the material.

The transformation temperatures of the Excel alloy observed in this study are relatively close to the ones for Zr-1Nb-1Sn-0.1Fe (Zirlo) and Zr-1Nb-1Sn-0.4Fe studied by Canay et al. [11]. The \( \alpha_{Zr} \rightarrow \alpha_{Zr}^+\beta_{Zr} \) transformation temperatures for these alloys is reported to be in the range of 960-973°C and the \( \alpha_{Zr}^+\beta_{Zr} \rightarrow \beta_{Zr} \) in the range of 650-741°C. It appears that the addition of extra 2.5% Sn and 0.8% Mo results in a net cancellation of the \( \alpha_{Zr} \)-stabilizing and \( \beta_{Zr} \)-stabilizing effects of Sn and Mo respectively. However, by calculating the volume fraction of \( \alpha_{Zr} \) and \( \beta_{Zr} \) phases in Canay et al.’s work, based on the chemical analysis results and partitioning of alloying elements at 850°C, one finds that there is
quite a considerable difference between Zr-Excel and these alloys (<40% and ~66% \( \beta \), respectively). Part of this difference could be due to the very low solubility of Nb in the \( \alpha \)-phase (<0.1%) reported in their study. This value seems rather inconsistent with results of other studies mentioned earlier which show the solubility limit of about 0.6%, which was also observed in the current study. Considering the fact that thin foil TEM samples were used for chemical analysis in this study as opposed to bulk samples (EMPA) in the Canay et al. study, it can be claimed that the chemical analysis results in this study are likely more reliable.

In summary the overall results of these three methods, i.e. quenching and metallography, DSC, and resistivity measurement for the \( \alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr} \) transformation temperature (in the range of 962-975°C) are in reasonable agreement. However, for the case of the temperature at which the volume fraction of \( \beta_{Zr} \)-phase starts to increase, the resistivity measurement shows a relatively higher temperature (above 700°C) compared to the other two methods (600-690°C).

The results of Quantitative EDS analysis (Table 3-2) show that Mo solubility in \( \alpha \)-phase (0.36-0.4 wt. %) is in agreement with the literature (<0.5 wt.%) [17] and the excess Mo concentrates in the \( \beta_{Zr} \)-phase; also the concentration of Nb in the \( \beta_{Zr} \)-phase is much higher than in the \( \alpha \)-phase which is quite close to the solubility limit of Nb in \( \alpha_{Zr} \) (0.6%). These two elements are known to be \( \beta_{Zr} \) stabilizers preventing the \( \beta_{Zr} \)-phase to transform into \( \alpha \) or \( \alpha' \) upon cooling. Figure 3-5 shows the Nb and Mo concentrations in the \( \beta_{Zr} \)-phase (wt.%) as a function of solution temperature. Clearly, as the volume fraction of \( \beta_{Zr} \)-phase goes up the corresponding concentrations of Nb and Mo decrease. It is known that in \( \beta_{Zr} \)-stabilized Zr alloys the martensite start (\( M_s \)) and finish (\( M_f \)) temperatures,
separated by a small gap in the range of 25 K for some investigated systems, lie in the \(\alpha_{Zr} + \beta_{Zr}\) region and they decrease with increasing solute concentration. Figure 3-10 shows a schematic pseudo-binary phase diagram of Zr-X alloys, X being \(\beta_{Zr}\)-stabilizer elements such as Mo and Nb in the case of Excel alloy. Superimposed on this phase diagram is the \(M_s\), \(M_f\) and \(\omega_s\) boundaries. According to this phase diagram, quenching from different temperatures in the \(\alpha_{Zr} + \beta_{Zr}\) region results in different microstructures. Quenching from high temperatures where the volume fraction of \(\beta_{Zr}\)-phase is high and therefore the concentration of \(\beta_{Zr}\)-stabilizing elements in the \(\beta_{Zr}\)-phase is low and the \(M_s\) is high, results in a fully martensitic transformation of the \(\beta_{Zr}\)-phase. However at lower temperatures the volume fraction of \(\beta_{Zr}\) is lower and it is richer in \(\beta_{Zr}\)-stabilizing solute elements. Since the \(M_s\) boundary has a very steep downward curvature with increasing solute content and probably reaches ambient temperatures, water-quenching from low temperatures won't result in martensitic transformation and instead, the microstructure of \(\beta_{Zr}\)-phase transforms into a mixture of athermal \(\omega\)-phase in a \(\beta_{Zr}\) matrix [6]. In the case of Excel alloy it appears that the combined concentrations of Mo and Nb have to be below a certain limit, in this case a combination of 1.46 and 1.42 wt. % respectively (at about 870°C), in order for the martensitic transformation to occur.
The TEM analysis in Figure 3-6 supports the above discussion. The SAD pattern is a complex one consisting of three individual patterns one of them with different variants. Each set of diffraction spots can be indexed knowing the crystal structure and lattice parameters of each phase. In the schematic SAD pattern reconstruction, the large filled circles are bcc \( <1\bar{1}0> \) zone axis reflections from the \( \beta_{Zr} \) matrix and the small squares are reflections from at least two variants of hexagonal (P6/mmm) \( \omega <1\bar{2}10> \) zone axis. Although the \( \omega \) particles are not visible in the micrograph, the SAD pattern clearly shows their presence and confirms the orientation relationship between \( \beta_{Zr} \) and \( \omega \), i.e. \( \{111\}_\beta \parallel (0001)_\omega; \quad <1\bar{1}0>_\beta \parallel <1\bar{1}20>_\omega \). The third set of reflections marked by arrows (not shown in the schematic) is from the martensite lath which seems to be orthorhombic.
α°. Hanson et al. [18] studied the β_{Zr}-phase transformation of some Zr-Th alloys and they found the following orientation relationship between orthorhombic α° and bcc β_{Zr}:

\[ [001]_{\alpha°} \parallel [110]_\beta, \ [100]_{\alpha°} \ 5° 16' \text{ from } [001]_\beta, \text{ and } [010]_{\alpha°} \ 5° 16' \text{ from } [110]_\beta. \]

The angular deviation from [001]_\beta and [110]_\beta axes for Zr-Excel alloy seems less, about 3-4°.

The ω-phase was first discovered in 1954 and it is known to have drastic effects on the mechanical properties of Zr and Ti alloys; the presence of ω in the microstructure considerably increases the strength and reduces the ductility. Studies on Ti-V alloys have shown a hardness as high as 600 HV due to the precipitation hardening effect of the ω-phase. Furthermore, studies of some Ti-Mo and Ti-V alloys have shown little or no loss of ductility or increase in yield strength upon formation of the ω-phase during either quenching or the early stages of aging [19].

In the case of Zr alloys, Aldridge and Cheadle have found that β_{Zr} in Zr-2.5Nb pressure tube material furnace-cooled or air-cooled from the α_{Zr}+β_{Zr} region, transforms into ω and enriched β_{Zr} as a result of aging in the temperature range of 300-500°C causing an increase in the hardness of the material. However the aging kinetics are very sluggish and the maximum hardness in their study was achieved after 2000-3000 hr aging. They attributed the high creep resistance of Zr-2.5Nb pressure tubes to the fact that aging of pressure tubes can be achieved in-situ at operating temperatures of CANDU reactors and it provides a strong network of ω and enriched β_{Zr} surrounding soft and ductile α_{Zr} grains acting as a barrier to dislocation movement [20] [21].
It has been reported that $\omega$-phase can be formed during deformation at room temperature, for example in quenched Ti-Mo, Ti-Cr and Ti-V alloys, however if the formation of martensite is more favourable it precedes the formation of $\omega$ [19]. Studies on Ti and Zr alloys (Zr-Mo-Al in particular) with stable $\beta$-phase at room temperature have shown that martensitic transformation can be induced in the retained $\beta$ by applying an external stress [6].

Considering the similarities between Zr and Ti alloy as well as the work done on Zr-2.5Nb alloy, one can expect to see similar behaviour in Excel alloy quenched from temperatures that allow retention of $\beta_{Zr}$-phase at room temperature, i.e. in the range 690-870°C; and it is possible to tailor the mechanical properties by controlling the volume fraction of retained $\beta$ and subsequent aging and/or cold working to obtain $\omega$ or martensite in the microstructure.

As a check for consistency of the volume fraction measurement and EDS data, Table 3-2 summarizes the results of quantitative EDS analysis on $\alpha_{Zr}$-phase and $\beta_{Zr}$-phase at 690°C, 800°C, 866°C, and 876°C; also the volume fraction of $\beta_{Zr}$-phase is given. Based on partitioning of the $\beta$-stabilizer alloying elements, i.e. Mo, Nb, and Fe, in the $\beta_{Zr}$-phase (EDS data from Figure 3-6) as well as in the $\alpha_{Zr}$-phase and the measured volume fractions, the overall wt% of these alloying elements were calculated, the result of which is given in Table 3-2. The results are in good agreement with the measured composition given in Table 3-1. The difference is mainly due to the volume fraction measurement which is more inaccurate in nature and to a lesser extent due to EDS data.
Table 3-2: Volume fraction of $\beta_{Zr}$ phase and the calculated overall concentration of the $\beta_{Zr}$-stabilizing elements based on partitioning of the elements in each phase

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\beta$ Volume Fraction (%)</th>
<th>Mo (wt. %)</th>
<th>Nb (wt. %)</th>
<th>Fe (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In $\beta$</td>
<td>In $\alpha$</td>
<td>overall</td>
<td>In $\beta$</td>
</tr>
<tr>
<td>690</td>
<td>19</td>
<td></td>
<td></td>
<td>4.05 ±0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.36 ±0.02</td>
</tr>
<tr>
<td>800</td>
<td>30.5</td>
<td></td>
<td></td>
<td>2.3 ±0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.25 ±0.02</td>
</tr>
<tr>
<td>866</td>
<td>44.5</td>
<td></td>
<td></td>
<td>1.46 ±0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2 ±0.06</td>
</tr>
<tr>
<td>876</td>
<td>65.5</td>
<td></td>
<td></td>
<td>1.22 ±0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.14 ±0.03</td>
</tr>
</tbody>
</table>

3.6 Conclusion

Three different methods, heating and quenching with subsequent metallography, differential scanning calorimetry (DSC), and resistivity measurement, were employed to study the phase transformation of Zr alloy Excel. From the heating and quenching experiment the $\alpha_{Zr} \rightarrow \alpha_{Zr} + \beta_{Zr}$ and $\alpha_{Zr} + \beta_{Zr} \rightarrow \beta_{Zr}$ transformation temperatures were found to be in the range of 600-690°C and ~968°C respectively; also the end of the stable $\beta_{Zr}$-phase was observed to be at ~864°C.

The $\alpha_{Zr} \rightarrow \alpha_{Zr} + \beta_{Zr}$ transformation temperature obtained from the DSC test is ~628°C, and the $\alpha_{Zr} + \beta_{Zr} \rightarrow \beta_{Zr}$ was found to be ~962°C during the heating cycle.

Resistivity measurement data shows the $\alpha_{Zr} \rightarrow \alpha_{Zr} + \beta_{Zr}$ to be ~745°C for the heating rate of 47°C/min which is significantly higher than the other two methods. The $\alpha_{Zr} + \beta_{Zr} \rightarrow \beta_{Zr}$
temperature was found to be between 975-979°C regardless of the heating rate which is in good agreement with the quenching experiment and DSC.

Transmission electron microscopy (TEM), selected area diffraction (SAD) pattern, and EDS study shows that at temperatures below ~870°C the concentration of $\beta_{Zr}$-stabilizer elements, i.e. Mo and Nb (1.46 and 1.42 wt% respectively) is high enough to prevent the transformation of $\beta_{Zr}$-phase into $\alpha'$-martensite. Instead the $\beta_{Zr}$-phase microstructure transforms into a mixture of athermal hexagonal (P6/mmm) $\omega$ and $\alpha''$-martensite in a matrix of $\beta_{Zr}$. 
3.7 References


Chapter 4
Aging Response and characterization of precipitates in Excel, a Zr alloy pressure tube material

Abstract
Precipitation hardening in Zr alloy Excel (Zr- 3.5 wt.% Sn- 0.8 wt.% Mo- 0.8 wt.% Nb) was studied using hardness testing and transmission electron microscopy (TEM). Solution treatment at 890°C, in the $\alpha+\beta$ region, and 980°C, in the $\beta$ region, followed by water-quenching and aging resulted in an increase of hardness, of up to 47% compared to the annealed material. The optimum condition for aging heat treatment was found to be 450°C and 1-2 hours. The precipitates were observed only in the transformed $\beta$ martensitic phase. Energy dispersive X-ray spectroscopy (EDS) in TEM showed the precipitate composition to be Zr-30wt.%Mo-25wt.%Nb-2wt.%Fe. Electron crystallography using whole pattern symmetry of the convergent beam electron diffraction (CBED) patterns together with selected area diffraction (SAD) polycrystalline ring pattern, suggests the $-6m\bar{2}$ point group for the precipitates belonging to hexagonal crystal structure, with an $a= 2.936 \text{ Å}$ and $c=4.481 \text{ Å}$, i.e. $c/a =1.526$.

4.1 Introduction
Zirconium alloys are used for casings of fuel bundles and are an important structural material in the core of nuclear reactors due to their low neutron capture cross section. The increasing demand for higher thermal efficiency means that coolant water must be used at higher temperatures and pressures. The Zr-2.5Nb alloy which is used for current pressure
tubes in CANDU reactors [1], does not have the required tensile and creep strength at temperatures approaching the 400°C envisaged in some future designs [2].

It is known that Zr-Sn-Mo-Nb quaternary alloys exhibit better mechanical properties than the Zr-Nb binary alloys [2][3], and among them Excel (Zr- 3.5% Sn- 0.8% Mo- 0.8% Nb)\(^1\) is a promising material for pressure tubes with high tensile strength and creep resistance[4]. In the annealed condition developed for current generation CANDU\(^\text{®}\) reactors Excel alloy is a dual phase material: \(\alpha\)-hcp and \(\beta\)-bcc with the volume fraction of 87% and 13% respectively. Most of its strength in the annealed condition is due to the solid solution strengthening effect of tin [2] and its fine grain size [5]. Furthermore, according to the Zr-Sn, Zr-Mo, and Zr-Nb binary phase diagrams precipitation hardening is potentially possible by solution treatment in the \(\alpha\)+\(\beta\) or \(\beta\) regions followed by quenching to produce a super saturated solution at room temperature and finally aging at high temperatures in the \(\alpha\) region to produce a fine dispersion of precipitates. If the solute atoms have low solubility in \(\alpha\)\(_{Zr}\), and segregate to the \(\beta\)\(_{Zr}\) as in the case of Mo and Nb, it is expected that precipitation will be observed in the transformed \(\beta\)\(_{Zr}\) (\(\beta\)\(_{Zr}\) after quenching) upon quenching from \(\alpha\)+\(\beta\) region. However, if the solubility of the solute atoms is higher in \(\alpha\)\(_{Zr}\) and segregate there, which is the case for Sn, precipitation is expected to happen in the \(\alpha\)\(_{Zr}\).

The Zr-Sn binary system with the Zr\(_4\)Sn+\(\beta\)\(_{Zr}\) \(\rightarrow\) \(\alpha\)\(_{Zr}\) peritectoid reaction at 962°C, has the potential for precipitation of Zr\(_4\)Sn intermetallics at room temperature for Sn concentrations above 3 wt% [6] [7] [8]. Douglass reported a significant increase in the yield stress and UTS of a Zr- 0.5% Nb- 3% Sn alloy due to precipitation of Zr\(_4\)Sn with

\(^1\) All compositions are in wt. % or wt. ppm unless stated otherwise
the precipitate volume fraction of up to 33% but there is no micrograph or chemical analysis in his paper to support this finding [9]. Carpenter et al. [10] showed that precipitation doesn't occur in binary Zr-Sn alloys with less than 9% Sn, and that age hardening due to Sn-rich precipitates was not achievable in dilute Zr-Sn alloys despite the fact that the phase diagram predicts it. Kwon and Corbett [11] studied the effect of oxygen on the stability of Zr₄Sn and found that at oxygen contents higher than 0.15 at% (248 wt. ppm) in the ternary Zr-Sn-O system, the Zr₄Sn intermetallic phase is not stable. Addition of iron even in small amounts (1.0-1.5 at.%) is known to have a similar effect on Zr₄Sn stability. In addition to the instability effect, oxygen is a strong α-stabilizer and expands the α region considerably, which in turn increases the solubility of Sn beyond aging temperatures [11].

The Zr-Mo binary system also shows the potential for precipitation, with the Mo₂Zr intermetallic phase forming from the β_{Zr} → α_{Zr}+ Mo₂Zr eutectoid reaction at 738°C [12]. Toffolon et al. [13] studied the pseudo-ternary Zr-Nb-Fe (1200 wt. ppm O) phase diagram with iron content varying from 150 wt. ppm to 5000 wt. ppm. They showed the presence of a Zr-Nb-Fe intermetallic phase with hexagonal crystal structure and the composition of 35%Zr-35%Nb-30%Fe in the alloys containing more than 0.3% Nb. They also found that the addition of Sn up to 2% had no effect on the composition of the precipitates or the phase diagram boundaries.

Thus according to all the binary and available ternary phase diagrams, one expects to see precipitation hardening in the Zr-Excel alloy quaternary system. In this study, the aging
response of the Zr alloy Excel and a characterization of the precipitates obtained is presented.

4.2 Material
An Excel alloy pressure tube provided by AECL Chalk River Nuclear Laboratories and designated XL 601 was used for this precipitation hardening study. The chemical composition of the tube is presented in Table 4-1. Figure 4-1 depicts the microstructure of the as-received pressure tube.

| Table 4-1 Chemical composition (wt. %) of the Zr-Excel alloy pressure tube |
|--------------------------|--------------|-------------|--------|--------|--------|------|------|
|                          | Sn           | Mo          | Nb     | O      | Fe     | H*   | Zr   |
| Spec.                    | 3.2-3.8      | 0.6-1       | 0.6-1  | 0.09-0.16 | 0.15  | 20 ppm | Balance |
| Measured                 | 3.39-3.68    | 0.77-0.81   | 0.75-0.77 | 0.11 | 0.09-13 | ≤5 ppm | Balance |

* The given H content is in the ingot; there might be up to 15 ppm H pickup during subsequent processing.
4.3 Experimental Procedure

At ambient temperatures Zr-Excel alloy is a dual phase material: α-hcp and β-bcc. It is necessary to know the phase diagram and transformation temperatures in order to design the aging heat treatment. The transus temperatures of Excel alloy were investigated in a previous study [14]. Based on the results of that study the $\alpha_{Zr} \rightarrow \alpha_{Zr} + \beta_{Zr}$, i.e. the temperature at which the volume fraction of stabilized $\beta$ starts to increase, and $\alpha_{Zr} + \beta_{Zr} \rightarrow \beta_{Zr}$ temperatures of respectively 600-690°C, and 970°C were used to guide the choice of solution treatment temperatures. The effect of the aging treatments on mechanical responses was assessed using Vickers hardness test. Microstructural observation and chemical analyses were done by TEM, STEM and EDS.

Samples with the approximate dimensions of 10x5x5 mm were cut from the pressure tube for aging heat treatments. The samples were ground with P200 sandpaper in order to remove the black oxide layer from the surface and then cleaned in an ultrasonic bath in
acetone prior to heat treatment. Temperatures of the samples were measured using an Inconel sheathed K-type thermocouple inserted into a drilled hole in the sample.

Three different solution treatments were designed to obtain different microstructures as follows: 1) solution treatment at 890°C followed by water quenching; this heat treatment gives a microstructure consisting of about 29% primary $\alpha_{Zr}$ and 71% transformed $\beta_{Zr}$ in the form of acicular martensite with hcp crystal structure, 2) Solution treatment at 980°C followed by water quenching which results in a 100% martensitic microstructure, 3) Solution treatment at 890°C followed by air cooling which produces a basket-weave Widmanstätten microstructure in the transformed $\beta_{Zr}$, with the same volume fraction of primary $\alpha_{Zr}$ as in the first heat treatment mentioned above [14].

The samples were then aged at 400, 450, and 500°C for 0.5, 1, 2, 3, and 4 hours. All the heat treatments were performed in flushing argon atmosphere with 99.999% purity inside a quartz tube in a LINDBERG/BLUE Mini-Mite™ tube furnace.

In addition, a sample solution treated at 890°C then water quenched was sealed in a glass tube under vacuum (10⁻³ Torr, roughing pump) and aged at 500°C for 550 hours in order to grow the precipitates for further transmission electron microscopy (TEM) analysis.

For hardness measurement, samples were mounted in epoxy with zirconia powder as filler. Samples were ground down to P1200 grit sandpaper before attack polishing by a solution of 5% HF, 5% HNO₃, 5% H₂O₂, and 85% distilled water mixed with 0.05 µm alumina slurry at an approximate ratio of 1:4.

Hardness of the samples was measured on the axial-radial cross-section of the tube employing a Buehler Macro-Vickers 5100 hardness testing machine to apply a 10kg load;
for each sample, hardness was measured at least at five different spots and the average result is reported.

Uniaxial tensile tests were done on two samples: 1) water-quenched from 890°C in the as-quenched condition, 2) water-quenched from 890°C and aged at 450°C for 1 hour. The samples were strained at a constant crosshead speed of 0.001 mm.s\(^{-1}\) equivalent to a nominal strain rate of about 10\(^{-4}\) s\(^{-1}\). The strain measurement was done by video extensometry using a 2448×2050 resolution digital camera.

Transmission electron microscopy was done on a Philips CM 20 TEM with a LaB6 filament and equipped with a Noran Vantage energy dispersive X-ray spectroscopy (EDS) detector; for scanning transmission electron microscopy (STEM) and EDS elemental mapping a JEOL 2010 microscope with a FEG gun equipped with an Oxford EDS detector was used. Sample preparation technique for TEM is described in [14].

A two-step replica extraction technique [15] was used in order to study the chemical composition of the precipitates without matrix interference in the samples quenched from 890°C and aged at 500°C for 550 hr. First, the samples were ground and attack polished according to the same procedure explained in [14]. Then, they were immerse etched in a solution of 5% HF- 35% HNO\(_3\)- 60%H\(_2\)O for 5-10 seconds. A strip of cellulose tape softened in acetone was applied to the sample making sure there were no air bubbles trapped under the tape and, after drying, it was peeled off. The side of the tape containing the precipitates was carbon coated in a JEOL JEE-400 Vacuum Evaporation instrument for about 8 seconds. Finally, the cellulose tape was dissolved in acetone and the carbon layer floating in acetone was collected using 200 mesh copper grids.
4.4 Results

Figure 4-2 shows the microstructure of the three different solution treatments explained earlier, namely: solution treated at 890°C followed by water-quenching (Figure 4-2.a), 980°C followed by water-quenching (Figure 4-2.b), and 890°C followed by air-cooling (Figure 4-2.c).

Figure 4-2  Figure 2  a) TEM micrograph of the sample water-quenched from 890°C. b) SEM and TEM (inset) micrograph of the sample water-quinched from 980°C. c) TEM micrograph of the sample air-cooled from 890°C
Figure 4-3a-c shows the results of aging response of the three different microstructures, i.e. water-quenched from 890°C, water-quenched from 980°C, and air-cooled from 890°C, plotted as the graphs of Vickers hardness (HV) versus aging time at different temperatures.
Figure 4-3 Hardness (HV) as a function of aging time for a) water-quenched from 890°C b) water quenched from 980°C c) air-cooled from 890°C. (error bars are standard deviation obtained from at least 5 measurements)
Presented in Figure 4-4 are the stress-strain curves of the samples water-quenched from 890°C in the as-quenched as well as aged (at 450°C for 1 hour) conditions. Table 4-2 summarizes the mechanical properties of these two microstructures.

![Engineering and true stress-strain curves](image)

**Figure 4-4**  a) Engineering and b)true stress-strain curves of the water-quenched samples from 890°C in the as-quenched as well as optimum aging (450°C for 1 hr) conditions.

**Table 4-2** Mechanical properties of two as-quenched and aged microstructures obtained from Figure 4-4. (error in Elastic modulus is based on 95% confidence interval of the best linear fit)

<table>
<thead>
<tr>
<th></th>
<th>Elastic Modulus (GPa)</th>
<th>0.2% Offset Yield Stress (MPa)</th>
<th>UTS (MPa)</th>
<th>Total Elongation, $\epsilon_f$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>890WQ-As quenched</td>
<td>60.46 ± 1.170</td>
<td>765</td>
<td>898</td>
<td>24</td>
</tr>
<tr>
<td>890WQ-Aged</td>
<td>73.6 ± 1.120</td>
<td>969</td>
<td>1145</td>
<td>9</td>
</tr>
</tbody>
</table>

Shown in Figure 4-5 is the bright field and dark filed TEM micrographs of the sample quenched from 890°C and aged at 500°C for 1 hour. Dark field micrographs clearly show
the precipitates about 10-20 nm in size inside the martensite laths (shown by arrows in the dark field micrographs).

Figure 4-5 Multiple beam bright field (left) and dark field (right) TEM micrographs of the sample water-quenched from 890°C and aged at 500°C for 1 hr showing the precipitates inside the martensitic phase; magnification: 100000x (top) and 175000x (bottom)
The results of STEM EDS elemental mapping on the over-aged sample quenched from 890°C and aged at 500°C for 550 hours is presented in Figure 4-6. The precipitates have grown to about 50 nm. The elemental maps show that they are rich in Mo, Nb, and Fe, and slightly depleted in Sn compared to the martensite matrix. Quantitative EDS analysis was performed on these precipitates as well as on the matrix (spectrum 1-5 on Figure 4-7) the results of which are reported in Table 4-3.

Figure 4-6 STEM micrograph of a region containing precipitates and the corresponding elemental maps for Mo, Nb, Fe, Sn, and Zr
Figure 4-7 STEM micrograph showing the same region as in Figure 4-6 and the spots where quantitative EDS was done; see Table 4-3

Table 4-3 Quantitative EDS analysis on the spots labeled Spectrum 1-5 in Figure 4-7. (wt. %)

<table>
<thead>
<tr>
<th></th>
<th>Zr</th>
<th>Mo</th>
<th>Nb</th>
<th>Fe</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>60.29</td>
<td>21.62</td>
<td>15.61</td>
<td>0.97</td>
<td>1.51</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>50.66</td>
<td>28.81</td>
<td>18.28</td>
<td>1.13</td>
<td>1.12</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>67.97</td>
<td>16.41</td>
<td>12.63</td>
<td>1.34</td>
<td>1.66</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>67.76</td>
<td>16.42</td>
<td>12.24</td>
<td>1.29</td>
<td>2.29</td>
</tr>
<tr>
<td>Spectrum (matrix)</td>
<td>94.92</td>
<td>2.03</td>
<td>0.25</td>
<td>0.18</td>
<td>2.61</td>
</tr>
</tbody>
</table>

Figure 4-8 shows an example of the TEM micrograph of the carbon replica extracted precipitates from the sample water-quenched from 890°C and aged at 500°C for 550 hours. The result of quantitative EDS analysis averaged over 12 spectra is presented in Table 4-4. The EDS spectra from the replicating carbon film was used as the background and subtracted from the precipitates’ EDS spectra.
Figure 4-8 TEM micrograph of the replica extracted precipitates (shown by arrows) from the sample water-quenched from 890°C and aged at 500°C for 550 hours

Table 4-4 Average chemical composition of the precipitates shown in Figure 4-8 obtained by quantitative EDS analysis

<table>
<thead>
<tr>
<th></th>
<th>Zr</th>
<th>Mo</th>
<th>Nb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. %</td>
<td>42.20</td>
<td>30.64</td>
<td>25.40</td>
<td>1.76</td>
</tr>
<tr>
<td>at.%</td>
<td>42.57</td>
<td>29.38</td>
<td>25.15</td>
<td>2.90</td>
</tr>
</tbody>
</table>

Presented in Figure 4-9 are three different zone axes convergent beam electron diffraction (CBED) patterns of the precipitates extracted from the sample water-quenched from 890°C and aged at 500°C for 1100 hours, showing the whole pattern symmetries which are used for the point group determination of the precipitates as described in the discussion section.
Figure 4-9 Convergent beam electron diffraction (CBED) patterns of the extracted precipitates from the sample water-quenched from 890°C and aged at 500°C for 1100 hr showing a) m (mirror plane) b) 2mm (2-fold rotation axis and 2 non-equivalent mirror planes) and c) 3m (3-fold rotation axis and 3 equivalent mirror planes) or 6mm (6-fold rotation axis and 2 non-equivalent mirror planes) symmetry.

Shown in Figure 4-10 is the selected area diffraction (SAD) ring pattern of the precipitates from the same sample as described above for Figure 4-9.
Figure 4-10 Selected area diffraction (SAD) polycrystalline ring pattern of the extracted precipitates from the sample water-quenched from 890°C and aged at 500°C for 1100 hr.

4.5 Discussion

In the case of the sample water-quenched from 890°C (Figure 4-3.a), the peak hardness at the aging temperature of 500°C occurs after 15 minutes (315 HV); it starts to decrease by about 10 HV after 1 hour, and finally it drops to 295 HV, halfway between the as-quenched condition and the maximum hardness, after 3 hours. This should be compared with the as-received material hardness, 232 HV. At 400°C, hardness reaches its maximum after a longer time, 2 hours, and it has started to decrease by 3 hours. The
maximum hardness at this temperature, 320 HV, is slightly higher than at 500°C. Finally, at 450°C the maximum hardness, 326 HV, is reached after 1 hour and it gradually drops by 3 hours; this is the highest HV number achieved after the three aging temperatures and is 40% higher than the as-received material hardness.

The sample water-quenched from 980°C follows a fairly similar trend (Figure 4-3.b). Aging at 500°C results in the maximum hardness of 327 HV after 1 hour and it starts to decline after 2 hours. However, at 400°C aging temperature the hardness is at its maximum, 330 HV, after 30 minutes and remains almost constant after 3 hours. Similar to the water-quenched sample from 890°C, the maximum hardness among the three aging temperatures (342 HV) is achieved at 450°C after 2 hours.

Finally, for the sample air-cooled from 890°C no significant change in hardness was observed as a result of aging heat treatment at 450°C and 500°C; the 30 HV increase in hardness compared to the as-received material is most likely due to the fine Widmanstätten microstructure (Figure 4-3.c).

The aging response of the water-quenched samples is very similar to the aging behaviour of the Zr-2.3% Mo binary system studied by Carpenter and Watters [16]. In their study they observed the peak hardness to occur at about 450°C after 1 hr. They also found that β-quenched Zr-2.5Nb shows almost no aging response on being subjected to the same aging treatment. By comparing their results with the current study, it can be concluded that the main precipitation hardening effect in Excel comes from Mo which initiates the precipitation and Nb contributes to the hardening by increasing the volume fraction of the precipitates.
A simple analysis of the tensile properties of both the as-quenched and aged microstructures given in Table 4-2 can be carried out to provide an understanding of the strengthening mechanism. Since there is no change in the grain size during aging it has no contribution to the strength and the only hardening effect is due to precipitation. Assuming a dislocation by-passing strengthening mechanism proposed by Orowan-Ashby (eq. 1) [17] one can calculate the increase in yield stress due to precipitation hardening:

$$\Delta \sigma = M \cdot \frac{0.13G b}{\lambda} \cdot \ln\left(\frac{r}{b}\right)$$

where $G$ is the shear modulus of the matrix, $b$ is the Burgers vector, $\lambda$ is the spacing between the precipitates, $r$ is the radius of the precipitates, and $M$ is the Taylor factor relating the normal stress in polycrystalline materials to single crystal shear stress.

For the purpose of this study, shear modulus of $\alpha$-Zr, 35.5 GPa [18], wouldn’t be a bad approximation for the shear modulus of $\alpha'$-hcp martensitic matrix. Also, taking the most common slip system in Zr, i.e. $\{10\overline{1}0\} <\overline{1}2\overline{1}0>$, as the operating slip system, the length of the Burgers vector would be 3.22 Å for Excel alloy. A Taylor factor of 3 for Zr can be used in the calculations [19].

The spacing between precipitates, $\lambda$, was estimated to be 50 nm from several TEM micrographs similar to Figure 4-5 using the mean linear intercept method. Also the average diameter of the precipitates is measured to be about 7 nm.

Substituting all the above mentioned values into the Orowan-Ashby equation, the increase in yield stress can be calculated to be about 210 MPa which is in good agreement with the experimental values in Table 4-2 showing an increase of about 204
MPa as a result of precipitation heat treatment. Therefore, it is likely that the observed increase in strength is due to the Orowan looping mechanism.

TEM micrographs in Figure 4-5 obtained in multiple beam condition, clearly show fine precipitates about 5-20 nm in size in the martensitic phase. The precipitates were observed both inside the martensite laths and on the grain boundaries between martensite laths. However, there was no evidence of Zr₄Sn precipitation in the α-phase. Referring to the Zr-Sn-Nb ternary phase diagram [9] one expects that by solution treatment at temperatures above 725°C the α-phase with the Sn and Nb contents of about 3.5% and 0.5% respectively (at 880°C), to be in the single phase alpha region. Therefore, quenching from the solution treatment temperatures should result in a supersaturated α-phase, and by aging at 500°C or below, at which the alloy is in the α+ Zr₄Sn two phase region according to the ternary phase diagram, precipitation of Zr₄Sn is expected to occur. The low concentration of Mo (0.3%) is unlikely to change the phase diagram boundaries drastically, so it's not likely to be the possible explanation for the absence of precipitates in the α-phase. In their study on the aging response of Zr-Sn alloys, Carpenter et al. [10] found almost no precipitation in the binary alloys containing up to 9% Sn. They suggested two possible reasons: 1- very slow kinetics of the precipitation process due to low diffusivity of Sn in Zr, which is almost similar to Zr self diffusion, or 2- incorrect phase boundaries of the reported phase diagram. The first possibility can be ruled out by the study of the over-aged sample at 500°C for 550 hours, as will be discussed below. One plausible explanation is the incorrect phase boundaries and hence higher solubility of Sn at low temperatures than predicted by the phase diagram. Also
oxygen is known to be a strong $\alpha$-stabilizer and oxygen pickup during solution treatment could expand the single $\alpha$-phase region to lower temperatures.

Due to the fineness of the precipitates, a sample water-quenched from 890°C was over-aged for 550 hours at 500°C for further characterization. The results of STEM EDS elemental mapping in Figure 4-6 show that the precipitates are rich in Mo, Nb and Fe. The quantitative EDS analysis on the large precipitates (~50 nm) showed that Mo, Nb, and Fe contents are about 21-28%, 15-18%, and 1% respectively. Also about 1.2-1.5% Sn was detected. In order to eliminate any contribution from the matrix in the EDS spectrum, precipitates were extracted using the replica technique and analyzed with EDS (Figure 4-8 and Table 4-4). The results confirm that there was some contribution to the EDS signal from the matrix and the composition of the precipitates obtained using the replica technique is Zr-30%Mo-25%Nb-2%Fe without any Sn detected. The chemical analysis in atomic percent given in Table 4-4 (Zr-29at.% Mo-25at.%Nb-3at.%Fe) suggests a stoichiometry of Zr$_3$(Mo,Nb,Fe)$_4$. The Fe content is much lower than the findings of Toffolon et al. [13] who found Zr-35% Nb-30% Fe precipitates in the Zr-Nb-Fe-Sn quaternary system suggesting the precipitation of a different intermetallic in Excel.

Due to its very low solubility in $\alpha$-Zr (<0.4%) [12], Mo has a strong precipitation hardening effect compared to other alloying elements such as Nb at the same concentration. However, it has a high neutron capture cross section, twice that of Nb for 1 wt. % addition to Zr, and therefore increasing the Mo concentration to higher than 1% is typically not considered for applications in the nuclear industry [2].

In order to determine the crystal structure of the precipitates, the whole pattern symmetry of the convergent beam electron diffraction (CBED) patterns was analyzed. Figures 4-9a
and 4-9b show two different zone axes CBED patterns with \( m \) (mirror plane) and \( 2mm \) (2-fold rotation axis normal to the plane of the diffraction pattern and two non-equivalent mirror planes) symmetry. The CBED pattern in Figure 4-9c shows a close packed arrangement of the diffraction disks which exhibits at least a \( 3m \) (3-fold rotation axis and 3 equivalent mirror planes) or \( 6mm \) (6-fold rotation axis and 2 non-equivalent mirror planes) symmetry. The exact symmetry of the CBED pattern in Figure 4-9c cannot be established due to very low intensity of the 1\(^{st}\) order Laue zone reflections.

From the above mentioned symmetries all the possible corresponding diffraction groups can be determined from the table of symmetries first published by Buxton et al. [20] as follows: \( m, m1_R, \) and \( 2Rmm_R \) for the \( m \) symmetry, \( 2mm, 2mm1_R, \) and \( 4Rmm_R \) for \( 2mm \) symmetry, \( 3m, 3m1_R, \) and \( 6Rmm_R \) for the \( 3m \) symmetry, and finally \( 6mm \) and \( 6mm1_R \) for \( 6mm \) symmetry. The subscript \( R \) in the diffraction groups means parallel to the plane of the diffraction pattern.

Consulting with the table of point groups [20][21][22] the only point groups that have one of each diffraction groups corresponding to the three different observed symmetries are \( 6/mmm \) and \( -6m2 \) which belong to the hexagonal crystal structure [23]. Therefore, the crystal structure of the precipitates can be narrowed down to the hexagonal structure with the space group falling in the category of \( P-6m2, P-6c2, P-62m, \) and \( P-62c \) for the \( -6m2 \) point group, and \( P6/mmm, P6/mcc, P63/mcm, \) and \( P63/mmc \) for the \( 6/mmm \) point group [23]. However, the exact space group cannot be inferred from these CBED patterns.

The selected area diffraction (SAD) pattern in Figure 4-10 shows polycrystalline Debye-Scherrer rings the radii of which are inversely proportional to the inter-planar spacing of the reflecting crystallographic planes. Knowing the camera constant of the TEM, the
inter-planar spacing corresponding to the rings numbered 1-6 in Figure 4-10 were
determined, the result of which is given in Table 4-5. The width of the brightest spots on
the diffraction rings were taken as a rudimentary estimate of the error in the measurement
of the rings’ radii which gives a maximum limit of uncertainty of ±0.03 Å for the d-
spacing of the first ring.

Based on the ratio of lattice parameters, the first three rings can be tentatively indexed as
(10\bar{1}0), (0002) and (10\bar{1}1) reflections which are common in all hexagonal crystal
structures. Solving for lattice parameters $a$ and $c$ based on the first two reflections
according to the equation for d-spacing in hexagonal crystal structures (eq. 2) [24], one
can then index the rest of the reflections accepting that there may be some very weak
reflections not showing up due to the higher intensity of the background. The rings 4-6
are indexed as (0003), (11\bar{2}1) and (10\bar{1}3), respectively.

$$\frac{1}{d_{hkl}^2} = \frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2} \quad (2)$$

Solving all the six reflections simultaneously to obtain a better fit of the lattice
parameters results in the $a$ and $c$ values of $2.936 \pm 0.024$ Å and $4.481 \pm 0.029$ Å
respectively\(^1\). The calculated d-spacings using the above mentioned $a$ and $c$ values for
reflections 1-6 are compared with the measured values in Table 4-5. Careful observation
of the ring pattern in Figure 4-10 also shows some faint reflection (marked by arrows)
which have a d-spacing of 1.68 Å corresponding to the expected (10\bar{1}2) crystallographic
planes.

\(^1\) The errors are standard error obtained from least square fitting of the experimental data
Table 4-5 Measured and calculated d-spacings of the diffraction rings 1-6 in Figure 4-10

<table>
<thead>
<tr>
<th>Diffraction ring/ (hkil) plane</th>
<th>1/(01(\tilde{1})0)</th>
<th>2/(0002)</th>
<th>3/(10(\tilde{1})1)</th>
<th>4/(0003)</th>
<th>5/(11(\tilde{2})1)</th>
<th>6/(10(\tilde{1})3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured d-spacing (Å)</td>
<td>2.57</td>
<td>2.25</td>
<td>2.13</td>
<td>1.49</td>
<td>1.40</td>
<td>1.29</td>
</tr>
<tr>
<td>Calculated d-spacing (Å)</td>
<td>2.54</td>
<td>2.24</td>
<td>2.21</td>
<td>1.49</td>
<td>1.39</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Calculating the allowed reflections for -6\(\tilde{m}\)2 and 6/mmm point groups using general structure analysis system (GSAS) [25] shows that the (0003) reflection is not allowed in the latter point group, while it is in the former. Hence based on the observed planes in the experimental selected area diffraction (SAD) ring pattern (Figure 4-10) we suggest that the point group of the precipitates is -6\(\tilde{m}\)2. This point group would also have (0001) allowed planes, however the d-spacing is so large that the diffraction ring would be obscured by the direct beam, hence cannot be observed.

With regard to in-reactor creep behaviour, Piercy [26] suggested that in irradiation creep mechanisms, such as irradiation enhanced climb of dislocations, in which flux of irradiation-induced point defects to dislocations is the rate controlling factor, the creep rate can be reduced by increasing the density of the sinks for point defects such as dislocation loops, defect clusters or solute atoms. Also it is proposed that precipitates can act as sites for recombination and annihilation of vacancies and interstitials [16]. Therefore, Piercy’s [26] argument about the competing effect of other types of sinks for point defects can be applied to precipitates as well.

Furthermore, if the in-reactor creep mechanism is climb-enabled glide in which the glide process is the strain producing step, a fine dispersion of precipitates can have a direct
effect on reducing the creep rate by reducing the distance that dislocations can move freely.

Based on the above argument it is worth studying the in-reactor creep behaviour of Zr-Excel alloy in the quenched and aged condition with a dispersion of very fine Mo-Nb rich precipitates which would be expected to exhibit low in-reactor creep rates.

### 4.6 Conclusion

The aging response of Zr alloy Excel was studied and precipitation hardening was observed in water-quenched samples solution treated at 890°C and 980°C. The optimum aging condition for both solution treatment temperatures was found to be 450°C and 1-2 hours. The increase in hardness was about 62 HV (23%) and 55 HV (19%) with respect to the as quenched condition and about 94 HV (40%) and 110 HV (47%) compared to the as received material for 890°C and 980°C solution treatment temperatures respectively. No aging response was observed in the air-cooled sample from 890°C. The precipitates size was of the order of about 5-20 nm distributed only in the martensitic phase. The chemical composition of the precipitates was determined to be Zr-30%Mo-25%Nb-2%Fe.

The Orowan-Ashby dislocation looping strengthening model estimates an increase in the yield stress which is close to the observed increase in strength and therefore is likely to be the strengthening mechanism observed in water-quenched and aged Excel. Electron crystallography using whole pattern symmetry of the convergent beam electron diffraction (CBED) patterns of the precipitates suggests the possible point groups of the precipitates to be \(-6m2\) or \(6/mmm\). Detailed comparisons of the lattice spacings observed
from the selected area diffraction (SAD) polycrystalline ring pattern, suggests the $-6m2$
point group for the precipitates, with $a= 2.936$ Å and $c=4.481$ Å, i.e. $c/a =1.526$.
There was no Sn-rich Zr$_4$Sn precipitate found either in the $\alpha$-phase or in the martensitic
phase, despite what might be expected from published phase diagrams. Therefore, the $\alpha$-
phase of this alloy does not seem to be precipitation hardenable.
4.7 References

Chapter 5
The Effect of Microstructure on High Temperature Mechanical Properties of Excel Alloy, a Pressure Tube Material for CANDU Reactors

Abstract
Tensile test and creep-rupture experiments at 400°C were performed to assess the effect of different heat treatments on the creep-resistance of Excel alloy (Zr- 3.5% Sn- 0.8% Mo- 0.8% Nb). The results suggest that a fully martensitic and aged microstructure has better creep properties at high stress levels (>700 MPa) while the microstructure from air-cooling from high in the $\alpha+\beta$ region is less sensitive to stress and shows better creep properties compared to the as-received annealed microstructure at lower stresses (<560 MPa). All the heat treated samples had a higher fraction of basal plane normals in the radial and axial direction of the pressure tube compared to the cold-worked and annealed microstructure which showed a typical strong transverse component in the basal pole figure.

5.1 Introduction
The Excel alloy (Zr- 3.5% Sn- 0.8% Mo- 0.8% Nb) is a promising material for CANDU reactors pressure tube due to its high strength and superior creep resistance [1][2][3]. It is a dual phase $\alpha$-hcp and $\beta$-bcc alloy with the approximate $\alpha$ and $\beta$ volume fractions of 87% and 13% respectively in the pseudo-equilibrium condition at room temperature [4]. Due to the presence of $\beta$-stabilizing elements, i.e. Mo, Nb, and Fe, the $\beta$-phase is stable at
room temperature [5]. Current pressure tubes are made from Zr-2.5% Nb which is quite satisfactory for the current design. However, in order to increase the thermal efficiency of CANDU reactors, the operating temperature and pressure of water coolant inside the pressure tube must be increased. Generation IV CANDU Super Critical Water (SCW) reactors are designed to have a maximum coolant temperature and pressure of 625°C and 25 MPa respectively (compared to 310°C and 10 MPa in the current reactors) in order to obtain a thermal efficiency of over 40%. In the re-entrant fuel channel design the coolant flows between the pressure tube and a concentric inner tube and at the end of the channel it turns around and flows through the inner tube in which the fuel bundles reside. In this design, the pressure tube operating temperature would be as high as 350-400°C [1]. Although at the current operating temperature and pressure, the thermal creep component of the total strain of pressure tubes is believed to be not more than 10%, it becomes more important at the high stresses and temperatures which are aimed for in future CANDU reactors and this puts a demand on higher strength and creep resistant materials [6].

Creep and in particular irradiation creep is one of the main life limiting factors in CANDU pressure tubes. It causes diametral expansion of the tube which in turn causes the coolant to bypass the fuel, reducing the thermal efficiency. Axial elongation of the tube as a result of irradiation creep can also lead to interference with other parts of the core components such as feeder pipes [2][3].

According to several studies on developing creep-resistant alloys for pressure tubes it was found that a composition in the range 3-4% Sn- 0.5-1.5% Mo- 0.5-1.5% Nb gives promising creep properties and higher strength with low neutron capture cross-section [3][7][8].
In their study on several Zr-Sn-Mo-Nb-Al alloys, Ibrahim et al. [8] found that the CX alloy (Zr-3% Sn- 1% Mo- 1% Nb) which is very close to Excel in composition, exhibits promising stress-rupture and thermal creep properties. At high stresses (294 MPa) and temperatures up to 300°C this alloy has an optimum stress-rupture and creep resistance in the water-quenched and aged condition with a microstructure of $\alpha'$ martensite with fine precipitates. However, at lower stress levels and higher temperatures they found that a microstructure of Widmanstätten $\alpha$ surrounded by a continuous network of $\beta$ produced by air-cooling from high temperatures in the $\alpha+\beta$ region gives the best creep properties.

Early studies on Zr-Excel alloy have shown that in the same metallurgical condition, Excel has a much higher tensile strength than Zr-2.5% Nb [2]. Also preliminary experiments on irradiation creep of Excel have shown that both in the extruded and stress relieved condition as well as extruded and cold drawn condition it exhibits lower creep rates than cold worked Zr-2.5% Nb [3]. Another study by Cheadle et al. [2] showed lower creep rates for Excel in all metallurgical conditions, i.e. cold worked and quenched and aged conditions, compared to Zr-2.5% Nb in the same condition. The creep rates of 5% cold-worked and annealed Excel tubes, derived from stress relaxation rates after 4000 hr at 297°C under 100 MPa stress in a neutron flux of $2\times10^{17}$ n.m$^{-2}$.s$^{-1}$, were found to be a half and a third respectively of the equivalent rates for Zr-2.5% Nb tubes. Also the difference between axial and transverse creep rates was similar to Zr-2.5% Nb indicating similar creep anisotropy (due to a similar texture).

Thermal creep and irradiation creep of pressure tubes are anisotropic processes due to the anisotropy of the $\alpha$-Zr hcp crystal structure as well as the crystallographic texture of the pressure tube. Current Zr-2.5% Nb CANDU pressure tubes are made by a hot extrusion
process which results in a strong texture with the basal plane normal of the $\alpha$-hcp grains predominantly oriented in the transverse-radial plane, more biased towards the transverse direction of the pressure tube. This particular texture causes the pressure tube to creep in the transverse and axial directions as a result of the biaxial stress state with the transverse stress twice that of the axial due to internal coolant pressure [6][9]. The in-reactor creep of the pressure tube is higher in the transverse direction but due to negative irradiation growth in the transverse direction the total transverse strain is less than in the axial direction [10][11]. In Zr-2.5Nb, changing the texture to increase the resolved fraction of basal plane normals in the radial direction, i.e. stronger radial component, while maintaining the concentration of basal plane normals in the radial transverse plane increases the transverse creep rate and decreases the axial creep rate [11]. According to Ibrahim and Holt [9] the total in-reactor strain of a randomized texture in which the basal plane normals are distributed evenly in the axial, transverse and radial directions of the pressure tube is expected to be reduced in the axial direction and increased in the transverse direction due to the axial component in the basal pole figure. In a texture with basal poles distributed only in the transverse-radial plane, strains can be negative while this is not the case for a random texture.

High temperature tensile properties of Zr alloy Excel pressure tube material will be presented here and stress-rupture tests have been employed to investigate the effect of different heat treatments on the creep properties. The heat treatments were designed to change the microstructure based on strengthening mechanisms such as precipitation hardening and grain size refinement, (reported in an earlier work) [12]. Also, the effect
of changing the crystallographic texture through the heat treatments will be discussed in this paper.

### 5.2 Material

A Zr alloy Excel pressure tube provided by AECL Chalk River Nuclear Laboratories with a designated number of XL601 was used in this study. The chemical composition, fabrication route, and microstructure of the as-received material are given in an earlier work [4]. The tube was extruded with an approximate ratio of 10:1, and cold worked about 25%. Then it was annealed at 750°C for 30 minutes and finally stress relieved at 400°C for 24 hours.

### 5.3 Experimental procedures

Three different heat treatments were developed to be tested as follows:

1- Solution treated at 980°C and water-quenched followed by aging at 450°C for 1 hour. At 980°C the microstructure is fully β-bcc which transforms into α’-hcp martensite upon quenching. Aging at 450°C for 1 hour results in the formation of very fine (~10 nm) Mo and Nb rich precipitates. Therefore, the final microstructure is fully martensitic with a dispersion of fine precipitates (Figure 5-1.a).

2- Solution treated at 890°C and water-quenched followed by aging at 450°C for 1 hour. 890°C lies in the α+β region with the α and β phases having an approximate volume fraction of 29% and 71% respectively [4]. Upon quenching the β-phase transforms into α’-hcp martensite while the α-phase remains unchanged. Aging heat treatment produces the same Mo and Nb rich precipitates in the martensitic phase as in the first heat
treatment; however no precipitation occurs in the $\alpha$-phase. The resultant microstructure consists of about 29% relatively soft $\alpha$-hcp and 71% hard $\alpha'$-hcp martensite with a fine dispersion of precipitates (Figure 5-1.b).

3- Solution treated at 890°C followed by air-cooling to room temperature and stress relieving at 450°C for 1 hour. Air-cooling results in the transformation of the $\beta$-phase into a combination of fine Widmanstätten $\alpha$-hcp grains with a continuous network of $\beta$-bcc along the grain boundaries. There is no precipitation as a result of the heat treatment at 450°C (Figure 5-1.c).

The heat treatments were carried out in a flushing argon (99.999% purity) environment and temperatures were monitored by a thermocouple probe inserted into a drilled hole inside the sample [4].

Tensile test samples with a rectangular cross-section of 4x2 mm$^2$ and a gauge length of 10.7 mm were machined from previously heat treated blanks cut in the axial and transverse directions of the pressure tube. Then the samples' surface were ground down to
P1200 sand paper in order to remove tool marks and the deformed layer and washed in acetone in an ultrasonic bath.

Because of the small size of the gauge region as well as high temperature of the experiments non-contact video extensometry and Digital Image Correlation (DIC) was used for strain measurement. For this purpose a 2448x2050 resolution digital camera and Dantec Dynamics Istra4D software were used. Images for stress-rupture tests and tensile tests were captured at an interval of 5 minutes and 5 seconds respectively. The Digital Image Correlation (DIC) technique is based on tracking points (pixels) in the images of the region of interest in the undeformed (reference) and deformed states. Instead of tracking single pixels, the reference image is divided into subsets centered on the point of interest. The subsets include a range of different grey scale pixels which make them unique and easily identifiable in the deformed image. The principle of image correlation is to find a displacement vector that matches the brightness distribution functions in the reference and deformed images [13][14].

Both the tensile tests and stress-rupture tests were done on a servo-hydraulic Instron 8502 universal tester. For stress-rupture tests, first the samples were heated to 400°C using an infrared heater keeping a constant pre-load of about 50 N on the sample (a stress of approximately 6MPa). After reaching the temperature the load was increased to the predefined constant value (80-92% UTS at 400°C) at a constant rate of 4 N/s (approximately 0.5MPa/s), at which load the sample was held until fracture.

The tensile tests were performed under a constant displacement rate of 0.001 mm/s equivalent to a strain rate of approximately $10^{-4}$ s$^{-1}$. 
Three thermocouples, one for controlling and two for recording the temperature were spot welded to the sample. The thermocouples were also used as high contrast tracking points for image correlation.

In order to reduce the oxidation, a quartz tube was put around the sample through which high purity argon (99.998%) was flowing.

The pre- and post-deformation texture of the room temperature tensile sample in the transverse direction in the uniform region of the gauge length was measured using electron backscatter diffraction (EBSD). The samples were mechanically and chemically polished according to the procedure described in an earlier work [4] prior to electropolishing in a solution of 5.3 g LiCl, 11.16 g Mg(ClO₄)₂, 100 ml butyl cellosolve, and 500 ml methanol at -35°C with a voltage of 50 V.

The textures of the as-heat treated samples mentioned above, as well as the texture of another sample that had been solution treated and water-quenched from 860°C, and of the as-received cold-worked and annealed material were measured by neutron diffraction. Water-quenching from 860°C results in a microstructure consisting of about 60% α-hcp and 40% retained β-bcc with ω-phase precipitates inside the β grains [4]. These texture measurements were made at a nominal wavelength of 2.075 Å obtained from the \{220\} reflection of a Ge single crystal monochromator, on the E3 spectrometer at the National Research Universal (NRU) reactor in Chalk River. Samples with a dimension of 3×9×9 mm were cut from the tube and stacked to form a cube of approximately 9 mm length side and wrapped in aluminum foil.
5.4 Results

5.4.1 Texture Measurement

Figure 5-2 depicts the basal pole figures\(^1\) of the samples water-quenched from 890°C and 980°C, air-cooled from 890°C. The textures of the quenched samples were measured in the quenched and aged condition. The resolved fraction of basal plane normals in the axial, radial, and transverse directions for each sample is given in Table 5-1.

![Figure 5-2 (0002) pole figure of a) 890°C air-cooled b) 890°C water-quenched c) 980°C water-quenched samples obtained from neutron diffraction. (All the samples were aged at 450°C for 1 hr)](image)

\(^1\) All the pole figures in this study are stereographic projection.
Table 5-1 Resolved fraction of basal plane normals in the axial, $f_a$, transverse, $f_t$, and radial, $f_r$, directions. (All the samples were aged at 450°C for 1 hr)

<table>
<thead>
<tr>
<th></th>
<th>As-received</th>
<th>890AC</th>
<th>890WQ</th>
<th>980WQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_a$</td>
<td>0.05</td>
<td>0.12</td>
<td>0.27</td>
<td>0.33</td>
</tr>
<tr>
<td>$f_t$</td>
<td>0.67</td>
<td>0.55</td>
<td>0.41</td>
<td>0.35</td>
</tr>
<tr>
<td>$f_r$</td>
<td>0.27</td>
<td>0.32</td>
<td>0.32</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Figure 5-3 shows the texture of the $\alpha_{Zr}$-phase and $\beta_{Zr}$-phase for the as-received sample as well as the sample water-quenched from 860°C.

Figure 5-3  (0002) pole figures of the $\alpha_{Zr}$-phase (left) and (110) pole figures of the $\beta_{Zr}$-phase (right) in the as-received condition (top) and water-quenched from 860°C (bottom)
5.4.2 Mechanical Properties

The results of room temperature tensile tests on the as-received Excel alloy pressure tube in the axial and transverse directions are shown in Figure 5-4. The room temperature mechanical properties of the as-received pressure tube obtained from Figure 5-4 are given in Table 5-2.

![Figure 5-4: Room temperature stress-strain curves of as-received Excel alloy in the a) axial and b) transverse directions](image)

Table 5-2: Mechanical properties of the as-received Excel alloy at room temperature\(^1\)

<table>
<thead>
<tr>
<th></th>
<th>E (GPa)</th>
<th>(\sigma_y) (MPa)</th>
<th>UTS (MPa)</th>
<th>(e_f) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial</td>
<td>120±3</td>
<td>577</td>
<td>726</td>
<td>20.85±0.07</td>
</tr>
<tr>
<td>Transverse</td>
<td>98.6±8.1</td>
<td>801</td>
<td>-</td>
<td>32.01±0.19</td>
</tr>
</tbody>
</table>

Presented in Figure 5-5 are the results of 400°C tensile tests on the as-received, 980°C water-quenched and aged, 890°C water-quenched and aged, and 890°C air-cooled and

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\(^1\) Errors in Elastic moduli throughout the text are calculated based on 95% confidence interval of the best fit linear trend. However the reported elastic moduli in this study might be subject to larger errors than suggested by these error bars; see discussion section
stress relieved samples in the axial and transverse directions. The mechanical properties obtained from 400°C tensile tests are summarized in Table 5-3.

Figure 5-5 400°C stress-strain curves for the as-received, 890°C air-cooled, 890°C water-quenched, and 980°C water-quenched microstructures. a) engineering stress-strain curves in the axial direction b) true stress-strain curves in the axial direction c) engineering stress-strain curves in the transverse direction d) true stress-strain curves in the transverse direction. (All the samples were aged at 450°C for 1 hr)
Table 5-3: 400°C mechanical properties of different microstructures. (All the samples were aged at 450°C for 1 hr)

<table>
<thead>
<tr>
<th></th>
<th>As-received</th>
<th>890AC</th>
<th>890WQ</th>
<th>980WQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (GPa)</td>
<td>Axial</td>
<td>Transverse</td>
<td>Axial</td>
<td>Transverse</td>
</tr>
<tr>
<td></td>
<td>43.7±2.8</td>
<td>58.4±2.0</td>
<td>54.1±6.2</td>
<td>37.1±1.6</td>
</tr>
<tr>
<td>(\sigma_y) (MPa)</td>
<td>335</td>
<td>471</td>
<td>420</td>
<td>555</td>
</tr>
<tr>
<td>UTS (MPa)</td>
<td>Axial</td>
<td>Transverse</td>
<td>Axial</td>
<td>Transverse</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>-</td>
<td>558</td>
<td>597</td>
</tr>
<tr>
<td>(\varepsilon_t) (%)</td>
<td>28.51±0.10</td>
<td>19.29±0.10</td>
<td>17.81±0.14</td>
<td>21.18±0.14</td>
</tr>
</tbody>
</table>

The results of creep-rupture tests are shown in Figure 5-6 as plots of stress\(^1\) as a function of time to rupture. The tests were carried out under constant load equivalent to the initial nominal stress levels presented.

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\(^1\) All the reported stresses for creep-rupture experiments are engineering stress
Figure 5-6 Creep-rupture graphs of different microstructures in the a) axial and b) transverse directions.

Figure 5-7 shows creep curves obtained from the creep-rupture tests performed on samples with the different microstructures mentioned earlier in the axial and transverse directions. The as-received material was not tested for creep-rupture in the transverse direction due to the very slow creep rates below yield point and immediate fracture above it.
Figure 5-7 Creep curves of a) as-received b) 890°C air-cooled c) 890°C water-quenched and d) 980°C water-quenched microstructures

Shown in Figures 5-8 is the log-log plot of secondary creep rates obtained from fitting a line to the secondary portion of the creep curves in Figure 5-7.
The reduction in cross-sectional area of the creep-rupture samples in the axial and transverse directions are tabulated in Table 5-4 and Table 5-5 respectively.

**Table 5-4 Reduction in area of creep-rupture samples tested in the axial direction**

<table>
<thead>
<tr>
<th>Stress (MPa)</th>
<th>As-received</th>
<th>890AC</th>
<th>890WQ</th>
<th>980WQ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>387</td>
<td>410</td>
<td>485</td>
<td>502</td>
</tr>
<tr>
<td>Reduction in area (%) - Axial</td>
<td>19.3</td>
<td>19.5</td>
<td>4.6</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Throughout the text 890AC, 890WQ, and 980WQ are abbreviations for air-cooled from 890°C and stress relieved, water-quenched from 890°C and aged and water-quenched from 980°C and aged respectively.
Table 5-5 Reduction in area of creep-rupture samples tested in the transverse direction

<table>
<thead>
<tr>
<th></th>
<th>890AC</th>
<th>890WQ</th>
<th>980WQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress (MPa)</td>
<td>537</td>
<td>561</td>
<td>670</td>
</tr>
<tr>
<td>Reduction in area (%) - Transverse</td>
<td>3.7</td>
<td>5.5</td>
<td>8.9</td>
</tr>
</tbody>
</table>

5.5 Discussion

5.5.1 Variant Selection

The strong axial component in the basal pole figure of the heat treated samples (Figure 5-2a-c) is a result of texture inheritance from high temperature \( \beta_{Zr} \) texture through the Burgers relationship. In zirconium and titanium alloys the Burgers orientation relationship, a crystallographic orientation relationship between \( \alpha \) and \( \beta \) phases when the alloy undergoes a phase transformation, states that \{0002\} planes in the \( \alpha \)-phase are parallel with the \{110\} planes in the \( \beta \)-phase and also \(<11\bar{2}0>\) directions in the \( \alpha \)-phase are parallel to \(<11\bar{1}>\) directions in the \( \beta \)-phase [15]. As a result of the Burgers orientation relationship there are six equivalent orientation variants during the \( \alpha \rightarrow \beta \) phase transformation and twelve variants during the \( \beta \rightarrow \alpha \) phase transformation. If all of the variants have the same probability of occurrence, then the final texture would be significantly randomized by an \( \alpha \rightarrow \beta \rightarrow \alpha \) phase transformation process [15]. However this is not the case and many researchers have reported either the retention/strengthening

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10 The reduction in cross-section is higher than total elongation in creep rupture test which could be due to error in cross-section measurement.
of the existing texture, i.e., a memory effect, or a strong texture after phase transformation, i.e., variant selection.

There are three suggested explanations for variant selection in the literature for a sample fully heated into the $\beta$ phase [15]: 1) internal stresses (either residual or transformation induced) stored in the high temperature phase due to volume and shape change bias the subsequent phase transformation behaviour; 2) thin films of the initial phase remain untransformed e.g. around precipitates which act as nucleation sites during subsequent phase transformation causing memory effect, 3) grain boundaries with specific orientation favourable for nucleation of certain variants are formed in the high temperature phase, and act as preferred locations for nucleation of $\alpha$ phase on cooling.

Wenk et al. [16] studied the phase transformation behaviour of hot rolled Zircaloy-4 and found that there is variant selection during the $\alpha \rightarrow \beta$ phase transformation and memory effect/texture strengthening during the $\beta \rightarrow \alpha$ phase transformation. The memory effect was attributed to growth of remnant untransformed $\alpha_{Zr}$, which is more likely the case or variant selection due to internal stresses induced by constraint imposed by neighbouring grains.

Romero et al. [15] observed that if the sample was only heated into the $\alpha + \beta$ phase field, an almost perfect memory effect was seen upon cooling to $\alpha$. Further they found no variant selection upon heating of rolled Zircaloy-2 fully into the $\beta$ regime, but did observe variant selection during subsequent cooling, where the $\alpha$ inherited the high temperature $\beta$ texture selectively during the $\beta \rightarrow \alpha$ phase transformation. Similar to Romero et al., Daymond et al. [17] also found no change in texture of Zr-2.5Nb pressure tube material if heated into the $\alpha + \beta$ region (but staying below the $\beta$ transus temperature)
and then returning to ambient conditions. However Daymond et al. did report significant variant selection during the $\alpha \rightarrow \beta$ phase transformation when heating above the $\beta$ transus temperature, as well as during the subsequent $\beta \rightarrow \alpha$ phase transformation. This variant selection led to the removal of the initial transverse (0002) intensity, which was replaced by strong axial (0002) intensity, in locations similar to that seen in Figure 5-2a), b) and c). The strong ‘cube’ like poles of the (0002) that are shown in Figure 5-2c) were associated in [17] with $\beta$ grain growth in the fully $\beta$ phase field.

Figure 5-2b and 5-2c show the basal pole figures of the samples water-quenched from 890°C (about 70% $\beta_{Zr}$ and 30% $\alpha_{Zr}$) and 980°C (100% $\beta_{Zr}$), respectively. These pole figures resemble the basal pole figures of Zr-2.5Nb in [17] after $\alpha \rightarrow$ fully $\beta \rightarrow \alpha$ using slow heating/cooling rate, hence a diffusional phase transformation. Starting with a predominant transverse component in the basal pole figure typical of pressure tubes (Figure 5-3) and assuming no variant selection, i.e. equal probability of all variants. The basal pole figure in the final texture after $\alpha \rightarrow \beta \rightarrow \alpha$ phase transformation is expected to resemble the theoretical (110) pole figure of the high temperature $\beta_{Zr}$ as shown in the predicted pole figures of Excel in Figure 5-9 as well as predicted pole figures of Zr-2.5Nb in Ref [17] and the theoretical pole figures of $\alpha_{Zr}$ shown by Cheadle and Ells [18]. A similar $\beta_{Zr}$ texture to this no-variant selection high temperature texture was observed at room temperature for the as-received Excel pressure tube and for the sample water-quenched from 860°C (which has about 40% stable $\beta_{Zr}$ at room temperature [4]), see Figure 5-3. This suggests epitaxial growth of the pre-existing $\beta_{Zr}$ grains during heating as opposed to nucleation and growth of new grains, a behaviour contrary to the observation of Daymond et al. [17] in the case of Zr-2.5Nb pressure tube material, where the initial
texture of the β-phase is very weak and random but it developed to a strong texture very similar to the β-phase texture of the sample water-quenched from 860°C (Figure 5-3), suggesting that in the Zr-2.5Nb the β-phase texture arose either due to growth of only a subset of the original β grains, or nucleation of new ones.

Comparing Figure 5-2b and 5-2c with Figure 5-9 shows that the two maxima at about 30° from the axial direction on the periphery are missing which indicates variant selection. Assuming that the β_Zr texture at 890°C and 980°C is the same as that at 860°C it is likely that this variant selection happens during quenching, i.e. β → α phase transformation. This assumption is based on the observation of Daymond et al. [17] in Zr-2.5Nb in which there was no significant change in the texture of β_Zr during heating in the α+β up to the fully β region.

Figure 5-9 Predicted pole figures of Excel during α → β → α phase transformation starting with the initial α texture shown in Figure 5-3 and assuming no variant selection; a) (110) pole figure of the β phase at high temperature b) (0002) pole figure of the final α phase
The variant selection observed in this study is contrary to the texture reported by Ibrahim and Holt [9] for a Zr-2.5Nb pressure tube water-quenched from 877°C (α+β region) which shows all the maxima for all variants indicating weaker variant selection, if any. Stanford and Bate [19] reported variant selection during quenching from the fully β_{Ti} region in the Ti-6Al-4V alloy. In their study the texture of the water-quenched sample showed all the maxima expected from no variant selection, however the texture strength was significantly higher for some maxima indicating variant selection. From EBSD studies they found that all the variants are present inside individual prior β_{Ti} grains; however the area fraction of each variant was different. The variant selection texture was modeled reasonably well based on shape change elastic strain interactions between neighbouring martensitic transformation products induced in the high temperature β_{Ti} matrix [20]. The same mechanism could also explain the variant selection during water-quenching of Excel. However, further detailed study and modeling is required to shed some light on this speculation.

Taking into account the volume fraction of α_{Zr} and β_{Zr} at 890°C, 29% and 71% respectively [4] (Figure 5-1.b), the resolved volume fraction of basal pole normals in the sample water-quenched from 890°C can be calculated from the initial as-received texture and texture of the sample water-quenched from fully β_{Zr} region, 980°C (Table 5-1). This results in \( f_α = 0.25, f_t = 0.44, \) and \( f_r = 0.31 \) which are in good agreement with the measured values in Table 5-1 which suggests that the transformation texture in both samples water-quenched from 890°C and 980°C are similar. However, the same calculation for the sample air-cooled from 890°C with the approximate post-transformation α_{Zr} and β_{Zr} volume fraction of 42% and 58% respectively (Figure 5-1.c)
results in $f_a = 0.21$, $f_l = 0.48$, and $f_r = 0.30$. Comparing the calculated $f_a$ and $f_l$ for this sample with the measured values in Table 5-1 ($f_a = 0.12$ and $f_l = 0.55$) suggests only a partial memory effect and some transformation texture with variant selection (the same components are missing as were missing in the water-quenched samples mentioned earlier). This is contrary to the previous studies on Zircaloy-2 [15] (with similar cooling rates to the current study) and Zr-2.5Nb [17] (with slower cooling rates) in which memory effect or texture strengthening were always reported upon cooling from the $\alpha+\beta$ region. The reason for this difference is not known, however the higher content of solute atoms with more sluggish diffusion rates than in Zircaloy-2 suggest that there might be some solute atom redistribution contribution to this phenomenon. In the case of the Excel alloy air-cooled from 890°C, the existing primary $\alpha_{Zr}$ grows during cooling, evidenced by higher volume fraction of $\alpha_{Zr}$ and larger grains compared to the sample water-quenched from 890°C (Figure 5-1.b and 5-1.c). In order for the primary $\alpha_{Zr}$ to grow it must reject the $\beta_{Zr}$-stabilizing element, Mo,Nb and Fe. However the faster cooling rate compared to the case of Zr-2.5Nb in the study by Daymond et al. [17], prevents the transformation to proceed fully by the growth of primary $\alpha_{Zr}$; since the transformation requires diffusion of the $\beta_{Zr}$-stabilizing elements. This could explain the difference observed between these two alloys and why no variant selection is observed in Zr-2.5Nb during cooling from the $\alpha+\beta$ region.

It should be mentioned that despite the observed variant selection, the crystallographic texture of the water-quenched samples are randomized compared to the initial as-received texture evidenced by $f_a = 0.33$, $f_l = 0.35$, and $f_r = 0.32$ for the sample water-quenched from 980°C.
5.5.2 Mechanical Properties

Before any discussion on the reported elastic moduli in Tables 5-2 and 5-3 it is necessary to discuss the reliability and accuracy of the data and employed method, i.e. static Young’s modulus. In a study on comparison between the ultrasonic technique and the conventional tensile test to measure the elastic modulus of 316 austenitic steel Ledbetter [21] found a fairly good agreement between the average values obtained from two techniques. However, the standard deviation of their tensile test results is about 12 times that of the ultrasonic technique with the gap between maximum and minimum values being 51 GPa. This shows that the statistical scatter in the conventional tensile test results is considerably higher which could explain the somewhat odd higher elastic modulus observed in the axial direction as well as the different results obtained in this study compared to those obtained by Pan et al. [22]. In a study on obtaining reliable modulus data, Lord and Morrell [23] reported a scatter as high as 70 GPa in the elastic modulus of BCR® Nimonic 75. In addition to stress and strain measurement accuracy, alignment of the whole tensile test apparatus is of great importance as a slight bend in the tensile sample can affect the modulus measurement. As a check for misalignment, strain should be measured on opposite sides of the gauge area, a practice which wasn’t employed in this study due to the particular test setup and strain measurement technique. Therefore the elastic moduli values obtained in this study should be considered for qualitative purposes only. They are not quantitatively reliable representative values for Excel, particularly because of the nature of the measurement and low statistics of the experiments; however they do show the expected trend of decrease in elastic modulus with increase in temperature.
Comparing Young's moduli of the as-received material at room temperature (Table 5-2) and 400°C (Table 5-3) shows the expected trend of decreasing elastic modulus with increasing temperature. However the elastic moduli at room temperature in the axial and transverse directions are not consistent with the crystallographic texture due to the possible sources of error mentioned above. According to the study of Fisher and Renken [24], the Young's modulus of $\alpha$-Zr is highest in the $c$ direction of the hcp crystal structure. The texture of the pressure tube (Figure 5-3) is such that $\alpha$-grains are oriented with their $c$ axis predominantly in the transverse direction. Therefore, contrary to the present observation it is expected to see higher values for elastic modulus in the transverse direction as was the case for Zr-2.5Nb pressure tubes studied by Pan et al. [22].

Employing the ultrasonic technique to measure the elastic modulus Pan et al. [22] [25] studied several Zr alloys including the Excel alloy from exactly the same pressure tube used in the present study with a designated number of 601 by AECL. They found a value of about 88 GPa and 70 GPa for the Young's modulus at 400°C in the transverse and axial direction respectively which is significantly higher than the current work's finding of 59 GPa and 44 GPa. This difference as well as the peculiarity of higher elastic modulus in the axial direction mentioned above could be explained by the different method used here.

The room temperature yield stress of the as-received material in the transverse direction, 801 MPa, is considerably higher than axial direction, 577 MPa, which is predicted from the strong transverse component in the (0002) pole figure. The axial direction yield stress is comparable to the value Christodoulou [26] found for Excel, however in his test the stress-strain curve exhibits a yield point drop which was not observed in this study. This
could be due to the constant crosshead speed control mode used in the current study which makes any possible yield drop difficult to detect because of relaxation in the load train. The obtained yield stress values are higher than those for Zr-2.5Nb pressure tube in the \( \alpha \)-annealed condition, which are about 300 MPa and 500 MPa in the axial and transverse direction respectively, obtained by Rodchenkov and Semenov [27]. The engineering stress-strain curve in the transverse direction (Figure 5-4) shows a continuous load drop after yielding until fracture. Therefore, the tensile strength can be taken as the yield stress. The initial drop and relatively flat portion of the true-stress vs. true-strain curve can be attributed to the occurrence of tensile twinning resulting in stress relaxation. Tensile twinning is one of the main deformation mechanisms when the applied load is parallel to the c-axis of \( \alpha \)-grains [28] which is the case in the transverse sample. This twinning mode causes the c-axis to rotate about 85 ° away from the tensile axis. Comparing the pole figures obtained from the undeformed and deformed transverse sample (Figure 5-10), there is an increased concentration of basal pole normals in the radial direction and considerably lower concentration in the transverse direction; this pattern of re-arrangement of the \{0002\} pole figure is typically associated with twinning. The slight rotation of the post-deformation pole figure around the transverse direction (Figure 5-10b) is probably due to misalignment of the sample with respect to the SEM coordinate system. Also the weak axial concentration in the EBSD pole figure of the as-received material (Figure 5-10a) is not visible in the neutron diffraction pole figure (Figure 5-3) due to contouring in the neutron diffraction pole figure; comparing the resolved volume fraction of basal poles in the axial direction obtained from EBSD (0.03) and neutron diffraction (0.05) shows that they are essentially the same. Shown in Figure
5-11 is an electron back-scatter diffraction (EBSD) map of the as-received, room temperature deformed sample in the transverse direction showing twinning particularly in large grains (indicated by red boundaries).

Figure 5-10 (0002) pole figures of a) as-received pressure tube and b) tensile tested in the transverse direction obtained from electron back-scatter diffraction (EBSD)
Figure 5-11 Electron backscatter diffraction (EBSD) map of the deformed transverse sample. (red boundaries show twins)

The 400°C transverse stress-strain curve exhibits a similar behaviour to that at room temperature, i.e. continuous decrease of the load after yielding. Again, the tensile strength can be taken as the yield stress. The same kind of behaviour, i.e. almost identical UTS and yield stress in the transverse direction, has been observed in α-annealed Zr-2.5Nb pressure tubes at room temperature as well as at 400°C. The 400°C yield stress and UTS of Excel is 471 MPa compared to 280-300 MPa for Zr-2.5Nb [27].

Dynamic strain aging (DSA) is a known phenomenon during uniaxial deformation of in Zr alloys at high temperatures. The manifestation of this phenomenon is a serrated plateau after yield point on the stress strain curve. Thorpe and Smith [29] reported dynamic strain aging (DSA) for Zr-1%Nb at 300°C. Kapoor et al. [30] reported DSA in
Zr-2.5Nb in the temperature range of 177°C-352°C. This behaviour is attributed to the clusters of oxygen atoms and their effect on pinning the dislocations in Zr alloys. It is likely that DSA occurs in the Excel alloy at the test temperature in the present study, 400°C, as well. However, due to slow strain sampling rate of the digital image correlation system, the occurrence of DSA was not confirmed in this study.

The room temperature yield stress of the as-received microstructure (Table 5-2) can be estimated within reasonable accuracy range based on the Hall-Petch [31] relation for grain size effect on strength:

\[ \sigma_y = \sigma_0 + kd^{-1/2} \]  \hspace{1cm} (1)

where \( \sigma_0 \) is called the friction stress and represents the resistance of the crystal lattice to dislocation movement at a theoretically infinitely large grain size, \( k \) is the temperature dependent Hall-Petch coefficient and \( d \) is the grain size.

Substituting \( k = 7.84 \text{ MPa.m.m}^{1/2} \) and \( \sigma_0 = 388 \text{ MPa} \) from Abson and Jonas’ [32] work on annealed Zr-3%Sn, and assuming an average grain size of about 1.5 micron obtained by linear intercept method for the as-received microstructure, one finds a yield stress of 589 MPa which is not far off from the observed value of 577 MPa.

It was shown in an earlier work [12] that the Orowan dislocation looping mechanism predicts the observed increase in room temperature yield stress (204 MPa) of the water-quenched and aged microstructures, due to the presence of fine precipitates, compared to the as-quenched condition, quite well. However, this mechanism only accounts for part of the observed increase in strength of the water-quenched and aged microstructure compared to the as-received condition (Table 5-3) and the grain size effect seems to be the other contributing mechanism.
The Hall-Petch coefficient $k$ for Zr at 400°C can be found to be about 2.5 MPa.mm$^{1/2}$ by extrapolating the $k$ vs. temperature line from Rodriguez’s work [33]. Banerjee et al. [5][34] studied the effectiveness of transformation micro-twins in water-quenched Zr-Ti alloys and found that the micro-twin boundaries are effective barriers to dislocation movement and the yield stress follows a Hall-Petch relation with the spacing between micro-twin boundaries, $\lambda$, replacing the grain size in eq. 1. The average spacing between micro-twin boundaries in the water-quenched and aged microstructures in this study is estimated to be about 70-80 nm from several high magnification TEM micrographs. Substituting these values into the Hall-Petch equation results in an increase of about 287 MPa. Adding 204 MPa due to Orowan looping gives an increase of about 491 MPa in the yield stress of the sample water-quenched from 980°C compared to the as-received microstructure which is quite close to the observed increase of 489 MPa (Table 5-3).

Considering the volume fraction of martensitic phase and primary $\alpha_{Zr}$ (about 70% and 30% respectively) and taking into account the negative contribution of grain growth of primary $\alpha_{Zr}$ (about 3.3 micron) in the microstructure water-quenched from 890°C, the increase in yield stress due to Hall-Petch effect can be calculated to be about 183 MPa. Taking into account the age hardening contribution, the total increase in yield stress can be estimated to be about 387 MPa which is again in good agreement with the observed increase of 395 MPa.

The same type of Hall-Petch analysis for the sample air-cooled from 890°C with the average Widmanstätten grain thickness of approximately 260 nm and the primary $\alpha_{Zr}$ grain size of about 4.5 micron results in an increase of about 95 MPa in the yield stress.
which is close to the observed increase of 85 MPa. In a study by Douglas [35] the effect of addition of up to 0.5% Nb to Zr-0.3% Sn alloy and addition of up to 0.9% Sn to Zr-0.1% Nb on the yield stress at 500°C was investigated. He reported almost no change in the yield stress at Sn and Nb concentrations higher than about 0.3%. The effect of Mo is expected to be similar since its atomic radius is very close to Nb (atomic number of 42 and 41 respectively). Therefore, solid solution strengthening due to solute redistribution in alpha and beta phases does not seem to play a significant role in the studied microstructures at high temperatures.

The strain at fracture at 400°C in the transverse direction, 19.29%, is less than that of room temperature, 32.01%. The same trend of decrease in total strain with initial increase in temperature in the transverse direction was reported for Zr-2.5Nb [27]. However in the case of Zr-2.5Nb the total strain starts to increase and becomes larger than the room temperature value (9%) above 300°C.

The 400°C UTS in the axial direction, 387 MPa, is lower than in the transverse direction due to the strong transverse texture of basal poles. However, Rodchenkov and Semenov [27] found almost the same UTS value in both axial and transverse directions in Zr-2.5Nb.

The results of 400°C tensile tests (Table 5-3) show a predictable trend for the investigated microstructures. The yield stress and tensile strength increase in order from as-received to 890°C air-cooled with equiaxed α and Widmanstätten microstructure, to 890°C water-quenched with equiaxed α and precipitation hardened martensite microstructure, and finally 980°C water-quenched with precipitation hardened fully martensitic microstructure. The ductility decreases in the same order, with the strain at
fracture of 890°C air-cooled sample (21.18%) being slightly higher than the as-received sample (19.29%) in the transverse direction. The anisotropy in mechanical properties, i.e. the difference between transverse and axial direction, becomes less in the same sequence of microstructures; for the 980°C water-quenched sample the yield stress in the axial and transverse directions are almost the same and the tensile strength in the axial direction is slightly higher than in the transverse direction. This is a result of change in the texture due to the different heat treatments.

For isotropic materials with random texture the axial in-reactor creep is expected to be zero [36]. Therefore all the heat treated microstructures in this study, with a more random texture than the typical pressure tube texture, are expected to have less in-reactor creep elongation. The texture of the fully martensitic microstructure with $f_a = 0.33$, $f_t = 0.35$ and $f_r = 0.32$, resembles that of the heat treated Zr-2.5Nb in a study by Ibrahim and Holt [9] with the Hill’s anisotropy parameters of $F = 0.674$ and $H = 0.799$ ($H-F = 0.125$) for the axial creep rate. Considering the similar texture of the fully martensitic Excel alloy and heat-treated Zr-2.5Nb [9] it is reasonable to assume a similar anisotropy parameter for the fully martensitic Excel alloy. Therefore, the axial creep rate is expected to be lower compared to the typical pressure tube texture which exhibits a greater difference in the anisotropy parameters, $H-F$.

Furthermore, the irradiation growth strain is correlated to the texture according to the equation in the general form of [9][37]:

$$G_d = 1 - 3f_d$$  \hspace{1cm} (1)$$

where $G_d$ is the growth anisotropy factor in the direction $d$ and $f_d$ is the resolved fraction of basal pole normals in the direction $d$. It is evident that the closer $f_a$ to 0.33 the less
axial growth of the pressure tube will be and a random texture with $f_a = f_i = f_r = 0.33$ results in zero irradiation growth. In the case of the heat treatments in the present study all the microstructures have higher $f_a$ than the as-received pressure tube; therefore it is expected that the axial irradiation growth would be less, particularly in the case of fully martensitic microstructure where $f_a \approx f_i \approx f_r \approx 0.33$; here the irradiation growth is expected to be zero. Another parameter that affects the irradiation growth behaviour is the grain size. It has been shown that the axial irradiation growth rate becomes negative for a pressure tube with a grain size smaller than 270 nm and $f_a = 0.03$, i.e. the standard pressure tube texture [10]. Therefore it is likely that for the heat treated microstructures in this study the grain size becomes an important factor in reducing the growth rate since the width of the martensite laths and Widmanstätten grains are in the range of 200-400 nm.

According to a study by Ibrahim and Holt [9] on a Zr-2.5Nb pressure tube with a similar texture to the heat treated textures in this study the in-reactor total strain in the transverse direction was predicted to be marginally lower than a pressure tube with typical texture while the axial strain was predicted to be an order of magnitude lower. Measurement of an irradiated heat treated Zr-2.5Nb pressure tube (same tube as mentioned in Ref [9] above) showed much lower elongation rate and slightly higher transverse strain rates compared to a cold-worked Zr-2.5Nb pressure tube with typical strong transverse component in the basal pole figure [38]. Therefore, a more randomized texture obtained in this study is expected to exhibit less in-reactor axial elongation.

The creep-rupture results in Figure 5-6 show that at relatively low stress levels the creep-rupture line of the as-received and 890°C air-cooled samples is very close to horizontal which means that the creep-rupture life of these two microstructures is very stress
sensitive. Noticeable in these two microstructures is the longer rupture time at higher stresses for the axial 890°C air-cooled sample compared to the as-received.

At fairly high stress levels exceeding the tensile strength of the as-received and the 890°C air-cooled samples, the 980°C water-quenched sample has better creep-rupture properties than the 890°C water-quenched sample indicated by longer rupture time despite higher stress levels. Also the water-quenched from 980°C microstructure is less sensitive to stress than the water-quenched from 890°C microstructure which implies that at lower stress levels its creep rupture resistance would be even better.

Assuming that either there is no change in the slope of the 980°C water-quenched line in the axial and transverse directions or it plateaus at lower stress levels (which is the likely case), it seems that its creep-rupture resistance may be better than or comparable to 890°C air-cooled microstructure at stresses about 450 MPa.

These results are in agreement with the findings of Ibrahim et al. [8] who found that for CX alloy (Zr-3%Sn-1%Mo-1%Nb) which is quite similar to Excel, that the optimum creep-rupture resistance at high stresses is achieved by a water-quenched and aged martensitic microstructure. However at lower stress levels an air-cooled Widmanstätten microstructure gives better creep-rupture properties.

In terms of steady-state creep rates (Figure 5-8) obtained from the linear secondary creep regime in Figure 5-7, it is evident that the 980°C water-quenched and the 890°C air-cooled samples exhibit the lowest creep rates both in the axial and transverse directions even though they were tested at higher stress levels compared to the 890°C water-quenched and as-received samples respectively. This further supports the creep-rupture results showing better creep properties of these two microstructures.
It was shown in an earlier work [12] on the aging response of Excel that the hardness of the water-quenched and aged microstructures starts to decrease after 3 hours aging at 400°C. Therefore it is expected that the studied microstructures overage at the test temperature and the precipitates lose their effectiveness in hindering dislocation movement.

In a study on irradiation induced microstructural changes in Zr-1%Sn-1%Nb-0.4%Fe Nikulina et al. [39] observed that the partially un-recrystallized microstructure becomes fully recrystallized after a fluence of $4 \times 10^{25}$ n.m$^{-2}$. Also the rhombohedral and hexagonal $(\text{Zr,Nb})_3\text{Fe}$ and Zr(Nb,Fe)$_2$ precipitates with the chemical composition of Zr-35-45%Nb 20-30%Fe were found to become depleted in Fe and transform to $\beta_{\text{Nb}}$ while new precipitates of Zr$_4$Fe and Zr$_3$Fe type formed after a fluence of $1 \times 10^{24}$ n.m$^{-2}$. However, there seemed to be no change in the Sn-rich precipitates probably in the form of tetragonal Zr$_4$Sn and hexagonal Zr$_5$Sn$_3$ observed in this material. It seems that the change in the precipitates is driven by irradiation enhancement of diffusion of interstitial Fe and therefore the composition of the precipitates observed in Excel with 2-3% Fe [12] are not expected to change as a result of irradiation.

Carpenter and Watters [40] observed that the hardness of $\beta$-quenched Zr-2%Mo increases considerably as a result of irradiation probably due to irradiation induced precipitation of Zr-Mo intermetallics, however this effect seemed to anneal out upon heating in the range of 300-500°C.

In general based on the above discussion irradiation is expected to drive the martensitic and aged microstructure towards equilibrium, i.e. an overaged and annealed
microstructure however it is not always the case that irradiated materials tend towards equilibrium.

The stress exponent, $n$, of the creep-rupture data, i.e. the slope of the $\log \dot{\varepsilon}$ vs. $\log \sigma$ (Figure 5-8) for the axial samples are 32, 78, 15, and 21 for the as-received, air-cooled from 890°C, water-quenched from 890°C, and water-quenched from 980°C microstructures, respectively. These exponents suggest that all the samples in the axial direction are in the power-law breakdown creep region. In the transverse direction the stress exponents are 53, 6.9, and 6.4 for the air-cooled from 890°C, water-quenched from 890°C and water-quenched from 980°C respectively. It is evident that similar to the axial direction the air-cooled microstructure is in the power-law breakdown region; however the water-quenched microstructures are in the power-law creep region exhibiting much lower stress exponents than in the axial direction despite the fact that they were tested at approximately the same stress levels, and that the texture of the water-quenched samples are randomized and hence one expects less anisotropy in these microstructure (as is evident from the tensile properties of the water-quenched microstructures). Since all the samples were tested at high stresses, the creep-rupture mechanism falls in the dislocation climb creep [41] category (according to the deformation mechanism map of $\alpha_{Zr}$) where the creep rate is controlled by the climb of dislocations. It should be pointed out that at lower stress levels encountered in creep the motion of dislocations is not as easy as in the high stress levels of creep-rupture. Hence the rate controlling mechanism switches from climb in creep-rupture to glide in creep [41]. Since the strain producing step in both the above-mentioned mechanisms is dislocation glide it is reasonable to assume that the
microstructures with better creep-rupture properties, i.e. air-cooled from 890°C and water-quenched from 980°C, will exhibit better creep properties as well.

The reduction in area after creep-rupture given in Tables 5-4 and 5-5 shows a higher ductility in the axial direction except for the 890°C air-cooled tested at 485 MPa and 980°C water-quenched tested at 734 MPa samples. Based on the very conservative creep-rupture limit of 5% strain for CANDU pressure tube design [10], the 980°C water-quenched and 890°C air-cooled microstructures should be studied in more detail at lower stress levels encountered in creep, if they are to be used for pressure tube microstructures. However, it should be mentioned that the very conservative creep-rupture limit of 5% strain is based on the data cold-worked Zircaloy-2 and Zr-2.Nb and applies to the current operating conditions of the CANDU reactors, i.e. stresses up to 200 MPa and stress exponent of $n=1$, which may not be the case for the Excel alloy at 400°C.

Figure 5-12 shows post deformation fractography on the creep-rupture samples. Despite the low reduction of area in some of the samples mentioned earlier, all the samples show dimples typical of ductile fracture. The only difference between the different microstructures is the dimple size which is much finer in the water-quenched martensitic samples, consistent with the grain size and the fact that grain boundaries are the most probable sites for micro-void nucleation. The most interesting feature in the fractography images is the inter-granular fracture mode in the 980°C water-quenched sample (Figure 5-12.d). This is likely due to grain boundary segregation of impurity elements such as Cl and P which are known to have deleterious effects on fracture properties of Zr alloys [42]. Pickles [43] studied the effect of grain size and hydrogen concentration on fracture resistance of Zr-2.5Nb pressure tubes. Two different microstructures were investigated:
1) water-quenched from $\alpha + \beta$ region and aged at 500°C with approximately 7% $\alpha$ having an average grain size of 15 micron. 2) water-quenched from $\beta$ and aged at 500°C with the grain size in the range of 50-500 micron. The results showed that hydrogen concentrations higher than 200 ppm have a more deleterious effect on fracture properties such as critical crack length and impact toughness, in the second heat treatment, which is quite similar both in the microstructure and grain size to the 980°C water-quenched sample in the present study. Therefore, according to the previous studies on Zr-2.5Nb, the coarse grain martensitic microstructure is likely more susceptible to hydrogen embrittlement which could be a limiting factor for its application.
In summary, among the four microstructures in this investigation, namely as-received annealed, air-cooled from 890°C, water-quenched from 890°C and aged, and water-
quenched from 980°C and aged, the last one shows better creep-rupture properties at high stresses and the air-cooled microstructure has better creep resistance at low stresses. Considering the conceptual design for CANDU-SCWR, the coolant pressure of 25 MPa induces an axial and transverse stress of 138 MPa and 278 MPa respectively, which are well below the yield stresses of these microstructures. Therefore, these microstructures are good candidates for high stress pressure tubes. The strength of the air-cooled microstructure can be further enhanced by increasing the solution treatment temperature to higher temperatures in the \( \alpha + \beta \) region in order to increase the volume fraction of the Widmanstätten phase in the microstructure. Also, in the case of the fully martensitic microstructure, theoretically better fracture resistance properties can be achieved by lowering the solution treatment temperature to high temperature in the \( \alpha + \beta \) region, for example 930-940°C, in order to reduce the prior \( \beta \) grain size.

5.6 Conclusion
Four different microstructures of Excel alloy were studied for high temperature tensile properties and creep-rupture resistance in this work. These are cold-worked and annealed (as-received pressure tube), air-cooled from 890°C followed by stress relieving at 450°C, water-quenched from 890°C followed by aging at 450°C, and water-quenched from 980°C followed by aging at 450°C.

The texture of all the heat treated microstructures showed less anisotropy with higher fraction of basal pole in the radial and axial directions compared to the cold-worked and annealed pressure tube with typical strong transverse component of basal pole figure.
The texture remained unchanged upon quenching from below 860°C, a temperature corresponding to retention of $\beta$–phase. However water-quenching or air-cooling from above this temperature results in change in texture and variant selection during cooling evidenced by strong axial component of the basal pole figure.

The water-quenched microstructures showed very high strength and low ductility while the air-cooled microstructure exhibited higher strength and comparable ductility to the cold-worked and annealed microstructure.

The creep-rupture results and the secondary creep rates showed that among all the microstructures the 980°C water-quenched and 890°C air-cooled have better creep properties at high stresses and relatively low stresses respectively.

Post-deformation fractography revealed that all the microstructures show dimples typical of ductile fracture despite very low reduction of area particularly in the water-quenched samples. There was evidence of intergranular fracture in the fully martensitic microstructure, most probably due to embrittlement of grain boundaries by segregation of impurity elements.
5.7 References

Chapter 6
Conclusion and Future Work

A summary of the results of the overall study is presented in this chapter. Also some suggestions for future work are provided at the end.

In order to design any thermal or thermo-mechanical treatments to achieve better mechanical properties it is necessary to know the transformation behaviour of the material under investigation.

Since there was no published phase diagram or any data on transformation behaviour of Excel, this study started with characterization of the transformation temperatures of Excel alloy using different techniques such as quantitative metallography, differential scanning calorimetry (DSC), and electrical resistivity measurement.

After finding the approximate $\alpha \rightarrow \alpha + \beta$ and $\alpha + \beta \rightarrow \beta$ transformation temperatures, different heat treatments were designed to assess precipitation hardening of the Excel alloy. These heat treatments include solution treatment high in the $\alpha + \beta$ and $\beta$ regions followed by water quenching and air-cooling (from $\alpha + \beta$ region) and subsequent aging at about 100-200°C below $\alpha \rightarrow \alpha + \beta$ transformation temperature. The aging response was assessed by hardness tests and tensile tests which showed a considerable increase in hardness and decrease in ductility of the water-quenched martensite microstructures. No aging response was observed in the air-cooled Widmanstätten microstructure.

Microstructural investigation showed fine dispersion of Mo-Nb-Fe-rich precipitates in the martensitic phase.

Texture measurement showed that all of the heat treated microstructures exhibit more randomized texture compared to the as-received typical pressure tube texture. This could
be beneficial in terms of in-reactor elongation of the pressure tubes which is due to strong
texture of the current pressure tubes as well as the inherent anisotropy of $\alpha_{Zr}$.

Finally, the developed microstructures were tested for creep-rupture properties. The
results showed good creep resistance for the heat treated microstructures at stress levels
exceeding tensile strength of the as-received pressure tube material. In particular the fully
martensitic microstructure showed exceptionally low creep rates at stress levels above
700 MPa. Also the air-cooled Widmanstätten microstructure showed low creep rates at
lower stress levels (<560 MPa).

Since the age-hardened martensitic microstructures show very little ductility they need to
be studied in more detail if they are to be used as pressure tube microstructures. Also
irradiation induced microstructural changes such as growth of the precipitates needs to be
studied in order to assess the stability of the precipitates during in-reactor operation.

Considering the lower stress levels encountered in the conceptual design for Generation
IV CANDU SCWR reactors (about 300 MPa transverse and 150 MPa axial) which fall in
elastic region of all the tested microstructures, the air-cooled Widmanstätten
microstructure shows a good combination of tensile strength, ductility, and superior creep
properties which makes it a promising microstructure for pressure tubes.

6.1 Summary

6.1.1 Chapter 3

Excel alloy is a dual phase material, $\alpha_{Zr}$-hcp, and $\beta_{Zr}$-bcc. Three experiments were
designed to study the phase transformation temperatures, namely heating and quenching
from different temperature followed by metallography and volume fraction determination
by manual point counting, differential scanning calorimetry (DSC), and resistivity change measurement.

The heating and quenching experiment was done in the temperature range of 600-970°C. The $\alpha_{Zr} \rightarrow \alpha_{Zr} + \beta_{Zr}$ transformation temperature, i.e. the temperature at which the volume fraction of stabilized $\beta_{Zr}$ starts to increase was found to be between 600-690°C corresponding to an increase in the volume fraction of $\beta_{Zr}$ from 13±0.5% to 19±2%. The $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ transus temperature was found to be approximately 968°C at which the microstructure after quenching is almost fully martensitic except some few isolated small $\alpha_{Zr}$ grains.

Differential scanning calorimetry (DSC) results show that the $\alpha_{Zr} \rightarrow \alpha_{Zr} + \beta_{Zr}$ and $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ transformation temperatures during heating cycle are ~628°C and ~962°C, respectively. These temperatures were obtained by finding the onset of non-linearity on the heat flow vs. temperature curve.

Finally, the resistivity change data shows that at a heating rate of 47°C/min, the $\alpha_{Zr} \rightarrow \alpha_{Zr}+\beta_{Zr}$ transformation temperature is ~745°C which is considerably higher than the other two methods. The $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ was found to be in the range of 975-979°C for the heating rates of 20°C/min and 47°C/min. The heating rate does not seem to have an effect on the $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ transus temperature.

Transmission electron microscopy (TEM), selected area diffraction (SAD), and EDS analyses on the heating and quenching samples showed that $\beta_{Zr}$-phase doesn't transform to $\alpha'$ martensite upon quenching from temperatures below ~860°C. This is due to the fact that at these temperatures the concentration of $\beta_{Zr}$-stabilizing elements, i.e. Mo and Nb is high enough to suppress the $\alpha'$ martensite-start temperature, $M_s$, to ambient...
temperatures. Instead, the $\beta_{Zr}$-phase microstructure transforms into a mixture of athermal hexagonal (P6/mmm) $\omega$ and $\alpha''$-martensite in a matrix of $\beta_{Zr}$.

6.1.2 Chapter 4

In the second manuscript the aging response of Excel alloy was studied. Hardness test was employed to assess the aging response of three heat treatments as follows: 1) solution treatment at 980°C and water-quenching followed by aging. 2) solution treatment at 890°C and water-quenching followed by aging. 3) solution treatment at 890°C followed by air-cooling and aging.

No aging response was observed in the air-cooled samples. The maximum hardness in both of the water-quenched heat treatments was achieved after aging at 450°C for 1-2 hours. TEM observation showed the presence of precipitates 10-20 nm in size distributed only in the martensitic phase. Replica extraction technique was used to study the chemical composition of the over aged precipitates (500°C for 550 hours) with the size in the range of 50-200 nm. EDS quantitative analysis showed the chemical composition of the precipitates to be Zr-30%Mo-25%Nb-2%Fe. No Sn-rich precipitate was found either in the $\alpha$-phase or in the martensitic phase. Therefore age-hardening in the $\alpha Zr$ via precipitation of $Zr_4Sn$ doesn't seem to be achievable despite the old published phase diagrams for Zr-Sn. However, recent studies on the solubility limits of Sn in $\alpha Zr$ show higher solubility which can explain the absence of Sn-rich precipitates in this study.

A simple analysis based on the tensile properties of the samples water-quenched from 890°C in the as-quenched condition as well as aged (450°C for 1 hr) condition, and the spacing between precipitates obtained from TEM micrographs by mean linear intercept
method, showed that Orowan-Ashby dislocation looping strengthening mechanism underestimates the observed increase in the strength due to precipitation hardening. Therefore, it is likely that the observed strengthening effect in the water-quenched and aged Excel alloy is due to a combination of coherency/semicoherency strains around the precipitates and precipitate shearing by dislocations.

Electron crystallography analysis based on whole pattern symmetry of different zone axis convergent beam electron diffraction (CBED) patterns of the over-aged (500°C for 1100 hr) and extracted precipitates suggests the possible point groups of the precipitates to be \(-6m2\) or \(6/mmm\), both belonging to the hexagonal crystal structure. Further analysis of the lattice spacings of the precipitates based on selected area diffraction (SAD) polycrystalline ring pattern suggests the \(-6m2\) point group for the precipitates, with an \(a=2.936\ \text{Å}\) and \(c=4.481\ \text{Å}\), i.e. \(c/a=1.526\).

Further discussion of Sn-rich precipitates in \(\alpha_{\text{Zr}}\) and recent observation in Excel is presented in the following.

Kuwae et al. [1] reported the presence of orthorhombic ZrSn, hexagonal Zr₅Sn₃, and body centered tetragonal pure Sn particles along the grain boundaries of Zircaloy-2 and Zircaloy-4 samples water-quenched from \(\alpha+\beta\) or \(\beta\) region which can not be explained by the Zr-Sn binary phase diagram and recent finding of Toffolon et al. [2] regarding relatively high solubility (about 6.4% at room temperature) of Sn in \(\alpha_{\text{Zr}}\). Woo et al. [3] reported irradiation induced precipitation of Zr₅Sn₃ intermetallic particles in Zircaloy-2 after neutron irradiation to a fluence of \(\sim 7.4\times10^{24} \text{n.m}^{-2}\) at a temperature of \(\sim 875\text{K}\). In the same paper Woo et al. [3] mention irradiation induced precipitation of Zr₅Sn₃ particles in Excel, however the results are not presented. They attribute this behaviour to irradiation-
enhanced substitutional diffusion of Sn in Zr and the strong interaction between vacancies and clusters of Sn atoms. They proposed that random annihilation of trapped vacancies by migrating interstitials such as Fe can inhibit solute emission from Sn clusters leading to rearrangement of Sn atoms to form Zr$_5$Sn$_3$ particles. However the presence Sn-rich precipitates in the water-quenched Zircalloys [1] suggest that the proposed mechanism by Woo et al. [3] for irradiation induced precipitation of Zr$_5$Sn$_3$ seems to be inaccurate.

The presence of Zr$_5$Sn$_3$ precipitates in Zircalloys suggest that the binary Zr-Sn phase diagram is not sufficient to explain quasi-binary Zr-Sn systems and other alloying elements and impurities such as Fe and oxygen even in very low concentration cause the Zr-Sn system to become a complex ternary or quaternary system.

6.1.3 Chapter 5

Texture of the heat treated samples (explained in the second manuscript) showed variant selection. In these samples some of the maxima in the basal pole figure are not present compared to the predicted pole figure for no variant selection. The $\beta$Zr texture of a sample water-quenched from 860°C (retained $\beta$Zr at room temperature) showed all the predicted maxima for no variant selection. This suggests that the observed variant selection in the water-quenched samples happens during $\beta$Zr $\rightarrow$ $\alpha'$ martensitic transformation assuming no change in the texture of $\beta$Zr at 890°C and 980°C. One possible mechanism for this variant selection could be shape change elastic strains interactions between neighbouring martensitic transformation products induced in the high temperature $\beta$Zr matrix.
Also in the case of air-cooled sample from 890°C ($\alpha_{Zr}+\beta_{Zr}$ region) only a partial memory effect was observed and some transformation texture with variant selection was observed which is contrary to previous reports on zirconium alloys heat treated in the $\alpha_{Zr}+\beta_{Zr}$ region.

High temperature tensile test and creep-rupture experiments at 400°C were performed on the developed microstructures explained in the second manuscript as well as on the cold-worked and annealed microstructure (as-received pressure tube). The 400°C tensile test results showed very high strength for the martensitic microstructure, i.e. UTS of 892-917 MPa and 815-832 MPa for the samples water-quenched from 980°C and 890°C and aged, respectively. However, the total elongation was quite low in the range of 3% and 6-12% for the above microstructures, respectively.

The air-cooled sample with Widmanstätten microstructure showed relatively higher tensile strength compared to the as-received annealed material with comparable ductility. The texture measurement showed less anisotropy for the martensitic samples with stronger axial and radial components in the basal pole figures compared to the as-received pressure tube typical texture with strong transverse basal pole texture. This fact is reflected in tensile properties in the axial and transverse directions which are less different for the martensitic samples compared to the as-received sample.

If we consider the potential application of the Excel alloy as a pressure tube material in the Generation IV Super Critical Water CANDU reactors (CANDU-SCWR), the air-cooled Widmanstätten microstructure seems to be the most promising microstructure, with a combination of relatively high strength, high ductility and low creep rate. The 400°C yield stress of this microstructure in the axial and the transverse directions (420
MPa and 555 MPa, respectively) are about 2.8 times and 1.8 times the designed stress, respectively (150 MPa and 300 MPa). However, the fully martensitic and aged microstructure shows low creep rates at higher stress levels, thus at the same stress level with the air-cooled microstructure it might show even lower creep rates. Therefore, it should not be ruled out merely based on its low ductility.

The observed increase in strength of the heat treated samples is consistent with the predictions based on Hall-Petch and Orowan looping mechanism.

The creep-rupture tests showed that 980°C water-quenched and 890°C air-cooled samples had the lowest creep rates. It is worth mentioning that the creep rates of the 980°C water-quenched sample were comparable to the 890°C air-cooled samples despite the fact that the stress levels were way beyond the UTS of the 890°C air-cooled samples. The stress exponent for all the samples were high, in the power law breakdown region except for the samples water-quenched from 890°C and 980°C which were in the range of power law creep despite the similar stress levels.

Fractography showed dimple shape fracture surface typical of ductile fracture for all of the microstructures. Evidence of intergranular fracture was observed in the fully martensitic microstructure with large grain size (200-600 micron) which is probably due to embrittlement of grain boundaries by segregation of impurity elements.

**6.2 Future Work**

An in-situ heating in-vacuo neutron diffraction experiment was proposed to study the transformation temperatures of Excel alloy. However, the experiment was delayed until recently. It was completed in January 2012 at National Research Universal (NRU) reactor
in Chalk River. The data will be analyzed and compared to the other three methods mention in Chapter 3.

The partial transformation of the $\beta$-phase upon quenching from temperatures below $\sim 860^\circ C$ which is mentioned in chapter 3 is an interesting microstructure for further studies to see whether it is possible to obtain any hardening in the $\beta$-phase by aging and growing the $\omega$-phase precipitates. It is suggested that transformation of the continuous network of $\beta$ into $\omega$ in Zr-2.5Nb pressure tube material is the reason for its good in-reactor creep-resistance. Furthermore, in-situ and ex-situ ion irradiation TEM investigation of this microstructure is in progress.

Regarding the transformation temperatures and precipitation in Excel alloy, thermodynamic modelling using available software and databases for calculations involving computational thermodynamics and diffusion controlled simulations such as Thermo-Calc [4] or FactSage [5] is necessary in order to fully understand the phase diagram.

Since the fully martensitic microstructure showed good creep resistance (Chapter 5), this microstructure needs to be studied in more detail and the only seemingly big problem, i.e. extensive grain growth of $\beta_{Zr}$-phase prior to quenching needs to be eliminated. Therefore, it is suggested to study the creep properties of samples water-quenched from just below the $\alpha_{Zr}+\beta_{Zr} \rightarrow \beta_{Zr}$ transformation temperature (940-950$^\circ C$) where the few isolated remaining $\alpha_{Zr}$ grains prevent the extensive growth of the $\beta_{Zr}$ grains. The creep properties could benefit from having an almost fully martensitic microstructure as well as small grain size.
Variant selection of Excel observed in this study is somewhat unique. Therefore, further detailed study of macro-texture as well as micro-texture using EBSD and microstructural investigation using TEM and comparison with Zr-2.5Nb at the same cooling rates seems necessary to shed some light on the mechanism of variant selection in Excel.

Finally, for the developed creep-resistant microstructure to be used in the nuclear industry, irradiation damage and in-reactor deformation as well as delayed hydride cracking (DHC) investigations are necessary.
6.3 References


Appendix A
Digital Image Correlation (DIC)

Digital Image Correlation (DIC) is a displacement mapping technique based on tracking points (pixels) in the images of the region of interest in the un-deformed (reference) and deformed states. Instead of tracking single pixels, the reference image is divided into subsets (facets) centered on the point of interest. The subsets (facet) include a range of different grey scale pixels which make them unique and easily identifiable in the deformed image. The principle of image correlation is to find a displacement vector that matches the brightness distribution functions in the reference and deformed images [1][2]. The principles of Digital Image Correlation (DIC) can be explained using the schematic in Figure A1.
Figure A-6-1 Schematic showing principles of Digital Image Correlation (DIC); the region of interest is divided into subsets (facets). The position of each facet is traced from un-deformed state (left image) to the deformed state (right image) [3]

In this Figure 1st image on the left refers to the un-deformed state and 2nd image on the right is in the deformed state. The image is divided into square subsets (facets) which will be tracked and located in the subsequent deformed image(s). Choosing the facet size depends on the contrast producing traceable features on the sample surface and is a somewhat trial and error process. Too large a facet size reduces the spatial resolution and too small a facet size results in few contrast producing features in each facet which makes tracking and one to one correspondence of the images difficult. To correlate the grey scale intensity of the images, different algorithms such as least square or Fourier transform can be employed.
In this study the high temperature test samples were ground to P1200 sand paper and therefore there were very little contrast features on the surface. However, three thermocouples were spot-welded to the gauge area of the tensile test (Figure A2) which provide enough local contrast. Since only average macro-strain was of interest, and also there was not enough contrast producing features on the whole gauge length, two regions of interest one at each end of the gauge length (where the thermocouples were spot-welded) were selected for image correlation. The facet size of 20 pixels was found to be the minimum size that can be used. Each facet was subdivided into grids of 5 pixel spacing at which strain was calculated. Then spacing between two points in each region of interest was used to calculate the strain.

Dantec Dynamic Istra4D software was used for image correlation in this study. For the tensile tests and creep-rupture tests images were captured at an interval of 5 seconds and 5 minutes respectively. Every next 20-30 image was used as reference image for subsequent images.
6.4 References


