MICROSTRUCTURAL STUDIES OF HEAT-TREATED Zr-2.5Nb ALLOY FOR PRESSURE TUBE APPLICATIONS

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OUTLINE

• Introduction
• Objective
• Background
• Optimization of Quenching Process
• Microstructural evolution in Ageing
• Texture and Mechanical Properties
• Conclusions
Pressure tube is the most critical life time core component in the PHWRs, which is subjected to harsh environment of high neutron flux, pressure and temperature.

Life of this component is therefore very important and it is expected that the pressure tube will be replaced once in the lifetime of the reactor.

Drawn Zr-2 pressure tubes were used initially. Later, pilger process was adopted for the cold working of extruded blanks. Subsequently, the material of construction was changed to Zr-Nb in view of its higher strength and lower hydrogen pick up rates during the reactor operation.
## TYPE OF PRESSURE TUBES USED IN INDIAN PHWRs

<table>
<thead>
<tr>
<th>REACTORS</th>
<th>TYPE OF PRESSURE TUBES</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPP - 1</td>
<td>DRAWN Zr-2 TUBES</td>
</tr>
<tr>
<td>MAPP - 2</td>
<td></td>
</tr>
<tr>
<td>NAPP - 1 &amp; 2</td>
<td>PILGERED Zr-2 TUBES</td>
</tr>
<tr>
<td>KAPP - 1</td>
<td></td>
</tr>
<tr>
<td>KAPP - 2</td>
<td></td>
</tr>
<tr>
<td>RAPP - 3 &amp; 4</td>
<td>PILGERED Zr –2.5% Nb TUBES</td>
</tr>
<tr>
<td>KAIGA - 1&amp;2</td>
<td></td>
</tr>
</tbody>
</table>

- REPLACEMENT CHARGES FOR RAPS –2, MAPS-1&2 AND NAPS - 1&2.
- FRESH CHARGES FOR TAPP - 3&4, KAIGA - 3&4.

- PILGERED Zr –2.5% Nb TUBES WITH IMPROVED CHEMISTRY
Zr-Nb Phase diagram

- Temperature (K)
- Atomic fraction of Nb

Phase regions:
- $\alpha + \beta_I$
- $\beta_I + \beta_{II}$
- $\alpha + \beta_{II}$

Temperature scale:
- 1200 K
- 1000 K
- 800 K
- 600 K

Atomic fraction of Nb scale:
- 0.2
- 0.4
- 0.6
- 0.8
- 1.0
Phase Transformations in Zr-Nb Alloys

**β\(_Zr\) (bcc)**

- **Slow Cooling**
  - \(α\) (hcp) + \(β\)\(_{Nb}\)
  - \(α'\) (hcp) martensitic <8%Nb Diffusionless

- **Rapid Cooling**
  - \(β\)\(_Zr\) + \(ω\)
    - 8-17%Nb Displacive
    - Retained \(β\)\(_Zr\) >17%Nb
    - \(β\)\(_Zr\) + \(ω\) or \(α\) (hcp) + \(β\)\(_{Nb}\)
  - Spinodal \(β\)\(_Zr\) + \(β\)\(_{Nb}\)

- **Ageing**
  - \(β\)\(_Zr\) + \(ω\) or \(α\) (hcp) + \(β\)\(_{Nb}\)
Creep rate of Cold Worked Pressure Tubes is found to be higher than expected.

Many studies and reactor experiences have shown that the heat treated Zr-2.5 Nb alloy pressure tubes in aged condition have better creep resistance than the cold worked pressure tubes.

India is going ahead with a large Nuclear Power Program, with PHWRs playing a vital role in the first stage. Therefore it is important to improve upon the creep resistance property to have longer life.
OBJECTIVE

- To develop Heat Treated Pressure Tubes with higher creep resistance for use in Pressurized Heavy Water Reactors and Advanced Heavy Water Reactors

&

- To optimize the thermo-mechanical treatment and establish a process flow sheet to manufacture Heat Treated Pressure Tubes on industrial scale.
Proposed Flow Sheet for Fabrication of Heat Treated Pressure tube

1. Quadruple vacuum arc melt ingot (Ø350 mm)
2. 1st Extrusion
3. Beta Quenching
4. 2nd Extrusion, ER=9.4:1, & Stress relieve at 480°C
5. 1st Pass Pilgering (41%CW)
6. α + β quenching
7. 2nd Pass Pilgering (23%CW)
8. Ageing at 515°C / 540°C for 24 hrs
9. Autoclaving (290°C for 120 hrs)
Metallurgical Factors affecting Creep Rate

- Microstructure
  - Grain Size
  - Grain Shape (Length:Width:Thickness)
  - Alpha/Beta Distribution
  - Beta Composition

- Texture

- Dislocation Density

- Chemical composition (Mainly Oxygen, Iron)
Quadruple vacuum arc melted ingot (Ø350 mm)

1st Extrusion

Beta Quenching

2nd Extrusion, ER=9.4:1, & Stress relieved 480°C

1st Pass Pilgering (41%CW)

α + β quenching

2nd Pass Pilgering (23%CW)

Ageing at 515°C / 540°C for 24 hrs

Autoclaving (290°C for 120 hrs)

AT QUENCHING:
1. SOLUTIONISING TEMPERATURE
2. COOLING RATE

AT AGEING:
TEMPERATURE
QUENCHING DILATOMETER STUDY
Aim:

- To accurately determine $\beta/\alpha+\beta_{Zr}$ transus temperature as a function of oxygen content

- To establish soaking temperature for obtaining a given level of $\alpha$ volume fraction

- To identify the quenching rate for obtaining fine martensitic structure
### CHEMICAL COMPOSITION OF MATERIAL USED FOR TRIALS

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %/ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niobium</td>
<td>2.68</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1137</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>28</td>
</tr>
<tr>
<td>Iron</td>
<td>650</td>
</tr>
<tr>
<td>Tin</td>
<td>25</td>
</tr>
</tbody>
</table>
Temp control = ± 0.1°C
Cooling rate controlled by Gas Quenching- 0.06 to 200°C/Sec
Thermocouple attached to the sample
ESTABLISHING SOAKING TEMPERATURE
COMPLETE HEATING AND COOLING CYCLE IN DILATOMETER
COOLING CYCLE IN DILATOMETER

Temperature in °C

Change in Length (Δl) in μm

First Inflection Point

$\beta \rightarrow \alpha + \beta_{Zr}$

Second Inflection Point

$\beta_{Zr} \rightarrow \alpha + \beta_{Nb}$

5°C/s
Cooling curve showing $\beta$ Transus Temperature

Maximum $\beta$ transus temperature = $891^\circ$ C.
SELECTION OF SOAKING TEMPERATURE

1. 883°C

2. 870°C
Microstructures after quenching at different rates (883°C/30 min)

- martensite
- Widmanstatten
- 100°C/sec
- 50°C/sec
- 25°C/sec
- 10°C/sec
Grain size prior $\beta \sim 10-15 \, \mu$m
Grain size $\alpha \sim 1-3 \, \mu$m
Primary $\alpha$ percentage $\sim 3$
Martensite plates $0.5-3 \, \mu$m

OIM-TEM Study Gas quenching (883°C/30min -100°C/sec)
Grain size prior $\beta \sim 10 \mu$
Grain size $\alpha \sim 1-3 \mu$
Primary $\alpha$ percentage $= 5-8$
Widmanstatten plates dimensions:
Length $= 10$ to $20\mu$
Width $\sim 1-2\mu$

OIM-TEM Study Gas quenching ($883^\circ C/30\text{min} -0.5^\circ C/s$)
<table>
<thead>
<tr>
<th>Cooling rate (°C/sec)</th>
<th>phase</th>
<th>Microstructural features</th>
</tr>
</thead>
</table>
| 100                   | α + Internally twinned martensite | Grain size prior β ~10-15 μm  
Grain size α ~1-3 μm  
Primary α percentage ~ 3%  
Martensite plates 0.5-3 μm |
| 50                    | α + Internally slipped martensite | Grain size prior β ~10 μm  
Grain size α ~1-3 μm  
Primary α percentage = 5–8%  
Widmanstatten plates dimensions:  
Length = 10 to 20μm  
Width ~ 1-2μm |
| 25                    | α + Widmanstatten | Grain size prior β ~10 μm  
Grain size α ~1-3 μm  
Primary α percentage = 5–8%  
Widmanstatten plates dimensions:  
Length = 10 to 20μm  
Width ~ 1-2μm |
| 10                    | α + Widmanstatten | Grain size prior β ~10 μm  
Grain size α ~1-3 μm  
Primary α percentage = 5–8%  
Widmanstatten plates dimensions:  
Length = 10 to 20μm  
Width ~ 1-2μm |
| 0.5                   | α + Widmanstatten | Grain size prior β ~10 μm  
Grain size α ~1-3 μm  
Primary α percentage = 5–8%  
Widmanstatten plates dimensions:  
Length = 10 to 20μm  
Width ~ 1-2μm |
Gas Quenched Microstructure (870°C/ 30 Mins)

100°C/sec

Martensite

50°C/sec

Martensite

25°C/sec

Widmanstatten

10°C/sec

α
## Microstructure Details (870°C/30 min)

<table>
<thead>
<tr>
<th>Cooling rate (C/sec)</th>
<th>phase</th>
<th>α vol. frac (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>$\alpha +$ Internally twinned martensite</td>
<td>15-20</td>
</tr>
<tr>
<td>50</td>
<td>$\alpha +$ Internally slipped martensite</td>
<td>15-20</td>
</tr>
<tr>
<td>25</td>
<td>$\alpha +$ slipped martensite</td>
<td>15-20</td>
</tr>
<tr>
<td>10</td>
<td>$\alpha +$ Widmanstatten</td>
<td>15-25</td>
</tr>
</tbody>
</table>
Microstructural observation

- **With decrease in soaking temperature from 883 to 870°C**
  - the cooling rate required for martensite formation is decreased from 50°C to 25°C/sec
  - α volume fraction increased from 5% to 20%

- **With decrease in Cooling rate**
  - Martensite morphology changed from twinned to lath martensite
  - Martensite laths became coarser
  - Widmanstatten plate width increased

Based on the above observations, it was decided to carry out full scale trials at 883°C
Extrude at 800°C (9.4:1 Extrusion Ratio) (123mm ODX 8 mmWT) & Stress relieved 480°C

Machining
120.0mm ODX 6.5 mm WT

1st Pass Pilgering (41%CW)
100.0mm ODX 4.5 mm WT

Heated in Vacuum & Water quenched at 883°C/30min

2nd Pass Pilgering (23% CW) 90.25mm OD X 3.8 mm WT

Ageing at 540°C for 24 hrs

Ageing at 515°C for 24 hrs

Autoclaving (290°C for 120 hrs)
The optical micrographs reveal banded structure. TEM micrograph shows the signature of dynamic recrystallisation.
Beta Quenched Microstructure (from 1000°C)

Optical Micrograph

Martensite needles of different generations in large prior beta grains

TEM Micrograph

Martensite contains very fine substructure
Microstructure after Final Extrusion

SEM Micrographs

Longitudinal

Transverse

TEM Longitudinal
Microstructure after 1st Pass Pilgering

SEM Micrographs

Transverse

Longitudinal

Pilgering operation retains the lamellar structure with fragmented beta

TEM Longitudinal micrograph showing highly cold worked structure
α + β quenched Microstructure of of 1st pass pilgered & Heat treated (WQ) 100mm OD x 4.5mm WT Tubes

883° C / 30min, WQ:

α=29% CW =41%
Quenching and deformation created a large number of nucleation sites for fine precipitation of $b_{\text{Nb}}$ phase.

Cold deformation of martensitic microstructure resulted in considerable increase in the dislocation density and dislocation substructure, which acted as nucleation sites for precipitation of $b_{\text{Nb}}$ from the supersaturated martensitic phase during subsequent ageing process.
Quenched and Aged Microstructures

Ageing 515°C/24 Hrs

SEM

40 - 45% Nb in β-Phase

TEM (Longitudinal)

Ageing 540°C/24 Hrs

75 - 80% Nb in β-Phase
## Textural Evolution

<table>
<thead>
<tr>
<th>Condition</th>
<th>$f_R$</th>
<th>$f_T$</th>
<th>$f_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>After second extrusion</td>
<td>0.29</td>
<td>0.61</td>
<td>0.10</td>
</tr>
<tr>
<td>As ($\alpha+\beta$) Argon quenched (883° C/30 Mins)</td>
<td>0.43</td>
<td>0.47</td>
<td>0.10</td>
</tr>
<tr>
<td>As ($\alpha+\beta$) water quenched (883° C/30 Mins) (lower effective quenching rate)</td>
<td>0.38</td>
<td>0.49</td>
<td>0.13</td>
</tr>
<tr>
<td>As ($\alpha+\beta$) water quenched (883° C/30 Mins) (higher effective quenching rate)</td>
<td>0.30</td>
<td>0.33</td>
<td>0.37</td>
</tr>
<tr>
<td>As aged 540°C/24 Hrs, (after WQ)</td>
<td>0.36</td>
<td>0.50</td>
<td>0.14</td>
</tr>
<tr>
<td>As aged 515°C/24 Hrs, (after WQ)</td>
<td>0.37</td>
<td>0.51</td>
<td>0.12</td>
</tr>
<tr>
<td>Cold work pressure tube</td>
<td>0.28-0.32</td>
<td>0.60-0.65</td>
<td>0.07-0.012</td>
</tr>
<tr>
<td>Tube Condition/Mech properties</td>
<td>UTS(MPa)</td>
<td>YS(Mpa)</td>
<td>% EL(1” GL)</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------</td>
<td>-----------</td>
<td>--------------</td>
</tr>
<tr>
<td></td>
<td>RT</td>
<td>HT (300C)</td>
<td>RT</td>
</tr>
<tr>
<td>Soaked at 883° C for 30 mins and Aged</td>
<td>749</td>
<td>494</td>
<td>581</td>
</tr>
<tr>
<td>540 C/24 hrs</td>
<td>770</td>
<td>497</td>
<td>560</td>
</tr>
<tr>
<td>515 C/24 hrs</td>
<td>735</td>
<td>502</td>
<td>553</td>
</tr>
<tr>
<td>CWSR pressure tubes (typical value)</td>
<td>735</td>
<td>502</td>
<td>553</td>
</tr>
</tbody>
</table>
The autoclave operation did not modify the microstructure to any noticeable extent.
Conclusions

- The first extrusion process produces uniform structure and completely breaks the cast structure. Second extrusion produces fine \((\alpha+\beta)\) lamellar structure.
- During \(\alpha+\beta\) quenching the soaking temperature determines the primary alpha volume fraction. Required cooling rate to obtain martensitic microstructure increases with soaking temperature.
- Ageing at 540°C resulted in fine \(\beta_{\text{Nb}}\) precipitates of equilibrium composition whereas; ageing at 515°C the \(\beta_{\text{Nb}}\) phase composition did not attain the equilibrium composition.
- Mechanical properties of the finished heat treated pressure tube aged at 540°C / 24 hrs. were similar to the cold work pressure tube. Tube aged at 515°C / 24 hrs was showing lower yield strength than that aged at 540°C.
The effect of quenching rates and soaking temperature on evolution of bulk crystallographic texture was studied. The primary alpha volume fraction had larger role in determining texture than the quenching rates. Sample water quenched with 5% volume fraction exhibited near random texture. Further deformation and ageing did not alter texture to any great extent.

- Fracture and Irradiation creep studies are required to be done to establish the new process route.
THANK YOU
### Design Conditions of Various Pressure Tube Type Reactors

<table>
<thead>
<tr>
<th>REACTOR</th>
<th>CANDU(6)</th>
<th>PHWR(220)</th>
<th>FUGEN</th>
<th>RBMK(1500)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Horizontal</td>
<td>Horizontal/Nat. U</td>
<td>Vertical</td>
<td>Boling water/ Vertical</td>
</tr>
<tr>
<td>Temperature</td>
<td>312 °C</td>
<td>312 °C</td>
<td>296 °C</td>
<td>290 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>12.7 Mpa</td>
<td>11.4 MPa</td>
<td>8 Mpa</td>
<td>8 Mpa</td>
</tr>
<tr>
<td>Flux level</td>
<td>$3.7 \times 10^{17}$ n/m².s</td>
<td>$3.7 \times 10^{17}$ n/m².s</td>
<td>$3.0 \times 10^{17}$ n/m².s</td>
<td>$2.6 \times 10^{17}$ n/m².s</td>
</tr>
<tr>
<td>PT material</td>
<td>CW Zr-2.5 Nb</td>
<td>CW Zr-2.5Nb</td>
<td>HT Zr-2.5Nb (WQ)</td>
<td>HT Zr-2.5Nb (TMT-1&amp;2)</td>
</tr>
<tr>
<td>Size</td>
<td>4.3mm WT 103.4 mm ID</td>
<td>3.3mm WT X 82.55mm ID</td>
<td>4.3mm WT 117.8 mm ID</td>
<td>4 mm WT 80 mm ID</td>
</tr>
</tbody>
</table>
### COMPARISON OF VARIOUS FABRICATION ROUTES FOR Zr-2.5Nb PRESSURE TUBES

<table>
<thead>
<tr>
<th>FABRICATION ROUTE</th>
<th>REACTOR</th>
<th>FABRICATION PROCEDURE IN BRIEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pilgered</td>
<td>Indian PHWR</td>
<td>Extrusion—Stress relieving—Pilgering—Intermediate Annealing—Pilgering—Autoclaving</td>
</tr>
<tr>
<td>Cold worked</td>
<td>CANDU 6</td>
<td>Extrusion—Cold drawing—Autoclaving</td>
</tr>
<tr>
<td>Heat treated TMT-1</td>
<td>RBMK-1500 (INPP-I)</td>
<td>Extrusion—Pilgering—Annealing—Pilgering—Annealing—Solution treatment—Cold working (23%)—Ageing at 515°C for 24 h—Autoclaving</td>
</tr>
<tr>
<td>Heat treated TMT-2</td>
<td>RBMK-1500 (INPP-II)</td>
<td>Extrusion—Pilgering—Annealing—Pilgering—Annealing—Solution treatment—Cold working (23%)—Ageing at 530°C for 24 h—Autoclaving</td>
</tr>
<tr>
<td>Heat treated</td>
<td>Fugen</td>
<td>Extrusion—Cold drawing—Solution treatment—Quenching—Straightening—Ageing at 500°C for 24 h.</td>
</tr>
<tr>
<td>Annealed</td>
<td>RBMK-1000</td>
<td>Extrusion—Solution treatment—Cold working (23%)—Annealing at 540°C for 5 h.</td>
</tr>
</tbody>
</table>
In-reactor dimensional changes of Zr-2.5Nb Pressure Tubes

\[ y = 0.0014x - 0.0003 \]

AHWR trend line with Fugen route

AHWR trend line with pilgered / CW route

AHWR trend line with TMT-1 route

Wolsong-1

AHWR trend line with Fugen route

Fluence / \( 10^{25} \text{ n.m}^{-2} \) (E>1MeV)
Creep rate of Cold Worked Pressure Tubes is found to be higher than expected.

<table>
<thead>
<tr>
<th>SL. NO.</th>
<th>FABRICATION ROUTE</th>
<th>DIAMETRAL CREEP STRAIN RATE, NORMALISED TO AHWR CONDITIONS (% PER YEAR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PILGERED (NFC)</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>COLD WORKED (CANDU)</td>
<td>0.26</td>
</tr>
<tr>
<td>3</td>
<td>COLD WORKED-ANNEALED</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>HEAT TREATED, TMT-1</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>HEAT TREATED, TMT-2</td>
<td>0.12</td>
</tr>
<tr>
<td>6</td>
<td>HEAT TREATED, FUGEN</td>
<td>0.12</td>
</tr>
</tbody>
</table>
High Speed Quenching Dilatometer
TEST SET UP & PARAMETERS

- A programmable and computer controlled induction heating furnace is provided to control the sample temperature within ±0.1°C.

- The induction coil is a double layered rectangular bore copper tube in which the inner layer provides the quenching gas while the outer layer is electrically connected to provide controlled induction heating.

- 0.1mm thick S type thermocouple is spot welded on the cylindrical surface of the specimen for accurate sample temperature measurement within ±0.1°C.

- The change in length and temperature of the specimen are recorded as a function of time during the experiment.
High Speed Quenching dilatometer

Instrument type: Bähr Dil 805 A
Manufacturer: Bähr-Thermoanalyse GmbH, Germany
Temperature range dependent on sample material: 20°C - 1500°C
Heating principle: inductive
Sample material: electrically conductive solid body
Atmosphere: inert gas, vacuum, air
Resolution: $\Delta l$ °C: 0.05 µm, 0.05°C

<table>
<thead>
<tr>
<th>Test Capabilities</th>
<th>Solid and hollow sample approx: d=4 mm, l= 10 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sample geometry</td>
<td>Max. 4000 K.s$^{-1}$ (hollow sample)</td>
</tr>
<tr>
<td>2. Heating rate</td>
<td>Typical for massive sample: 20 K.s$^{-1}$</td>
</tr>
<tr>
<td>3. Cooling rate</td>
<td>Max : 2500 K.s$^{-1}$ (hollow sample)</td>
</tr>
<tr>
<td></td>
<td>60 K.s$^{-1}$ (massive sample)</td>
</tr>
</tbody>
</table>
Trial experiments were carried out prior to the actual CCT study on Zr-2.5%Nb PT to determine the following:

- Optimum quenching rates achievable under vacuum
- Optimum quenching rates achievable using He
- Effect of heating rate on the transformation temperatures during heating
- Effect of annealing at 450°C for different duration
- Time for homogenisation at 1050°C
- Specimen surface oxidation
- To study the dilation behaviour during repeat runs on the same specimen
Temperature program for quenching dilatometry

The heating program:

- Heating from RT at 30°C/min up to 450°C
- soaking at 450°C for 60 minutes to relieve residual stress due to machining stresses
- Heating rate from 450°C to 1050°C at 5°C/min
- β-homogenising treatment at 1050°C for 30 min
- final quenching at different rates.

Quenching rates varied in the range of 0.06 - 100°C/s.