Chapter 3

Materials and Methodology

This chapter describes details of materials used, experimental methods and characterization techniques used during this study. The computational technique used for modeling microstructure evolution during diffusional phase transformation is also discussed.

3.1 Material

Two series of Zr base alloys were used. The alloys of Zr-Sn-Fe-Cr series, were triple arc melted ingot which were manufactured at Nuclear Fuel Complex (NFC) Hyderabad. One alloy containing 1.53 wt. % Sn and the other one having 1.35 wt. % Sn with transition elements as given in table 3.1. These were having composition of optimized Zr-Sn-Fe-Cr series alloy and designated as alloy 1, alloy 2 respectively in the thesis.

Table: 3.1 Chemical composition of two Zr-Sn-Fe-Cr alloys

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Sn* (wt.%)</th>
<th>Fe* (wt.%)</th>
<th>Cr* (wt.%)</th>
<th>Fe+Cr (wt.%)</th>
<th>O# (ppm)</th>
<th>C** (ppm)</th>
<th>Si** (ppm)</th>
<th>N** (ppm)</th>
<th>H** (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy1</td>
<td>1.53</td>
<td>0.20</td>
<td>0.10</td>
<td>0.30</td>
<td>1007</td>
<td>100</td>
<td>65</td>
<td>39</td>
<td>5</td>
</tr>
<tr>
<td>Alloy2</td>
<td>1.35</td>
<td>0.19</td>
<td>0.09</td>
<td>0.28</td>
<td>1064</td>
<td>78</td>
<td>42</td>
<td>30</td>
<td>4</td>
</tr>
</tbody>
</table>

* Error in estimation 0.1%

# Error in estimation 1%

** Error in estimation ±1 ppm

Another series of alloy chosen is Zr-Nb series. Cold worked stress relieved Zr-2.5Nb pressure tubes fabricated at NFC, Hyderabad, were used in this study. The fabrication flow-sheet [3.1] of pressure tube is given in fig. 3.1. Coupons sliced from tubes just after autoclaving were used as
starting material and are referred to as-received material. To study the effect of Fe content in Zr-Nb-Fe alloy on microstructure and precipitates characteristics and in turn its oxidation and hydrogen pick up behavior of the alloy, three different compositions (table 3.2) of Zr-2.5Nb pressure tubes were selected. These alloys were having Fe-content of 300 ppm, 800 ppm, 1250 ppm and were designated as alloy 3, alloy 4 and alloy 5 respectively.

![Fabrication flow sheet for production of seamless Zr-2.5%Nb pressure tubes for PHWR at NFC, Hyderabad](image)

Fig. 3.1 Fabrication flow sheet for production of seamless Zr-2.5%Nb pressure tubes for PHWR at NFC, Hyderabad [3.1]
3.2 Sample preparation and different characterization techniques:

3.2.1 Fabrication of coupons and thermo mechanical treatment:

Samples from triple melted ingot of Zr-Sn-Fe-Cr were initially 30% cold rolled and 10-15% cross rolled to break the previous cast structure. Then these samples were cut into small pieces and encapsulated in glass tube under helium environment. Solution annealing was carried out at 1050° C for 30 min and immediately glass capsules were transferred and broken into water to achieve high cooling rate. Quenched samples were again encapsulated in quartz glass tube with helium gas filled at 100mm Hg pressure and α annealing heat treatment was carried out at 700°C and 800° C for 15 mins, 1hr. and 10 hrs., respectively to study size, size distribution and nature of the SPPs. To observe the effect of annealing at α+β phase field, annealing of some samples was carried out at 850°C for 1 hr.

A mathematical parameter which is a combination of time and temperature of each annealing heat treatment to sum up effect of all applied heat treatment in the α phase region of zirconium during fabrication, is described as Cumulative Annealing Parameter (CAP) [3.2],

\[
CAP = \sum_{i=1}^{N} A_i = \sum_{i=1}^{N} t_i \exp\left(-\frac{Q}{RT}\right)
\]  

-------------------  3.1

Table: 3.2 Chemical Compositions of the Zr-Nb series

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nb (wt%)</th>
<th>Fe (ppm)</th>
<th>O (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy-3</td>
<td>2.60</td>
<td>300</td>
<td>946</td>
</tr>
<tr>
<td>Alloy-4</td>
<td>2.47</td>
<td>800</td>
<td>950</td>
</tr>
<tr>
<td>Alloy-5</td>
<td>2.49</td>
<td>1250</td>
<td>1003</td>
</tr>
</tbody>
</table>
taking Q/R =40000 K. A wide range of CAP (in hrs.) values were calculated (Table 3.3) for each annealing heat treatment.

Table: 3. 3 CAP values for each alpha annealed heat treated condition

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Annealing Condition</th>
<th>CAP in hrs.(Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>700° C for 15 mins.</td>
<td>0.35x10^{-18}</td>
</tr>
<tr>
<td>2.</td>
<td>700° C for 1 hr.</td>
<td>1.4x10^{18}</td>
</tr>
<tr>
<td>3.</td>
<td>700° C for 10 hrs.</td>
<td>14x10^{18}</td>
</tr>
<tr>
<td>4.</td>
<td>800° C for 1 hr.</td>
<td>64.6x10^{-18}</td>
</tr>
<tr>
<td>5.</td>
<td>800° C for 10 hrs.</td>
<td>646x10^{-18}</td>
</tr>
</tbody>
</table>

To study the influence of β phase on corrosion and hydrogen intake behaviour of Zr-2.5Nb alloy higher volume fraction of β(Zr) phase was generated in the as received samples (alloy 5) after soaking the material at 680°C for 2 hrs. i.e. above monotectoid temperature and followed by air cooling. The heat treatment was carried out in ‘He’ environment keeping the samples in encapsulated quartz glass tube. This sample is designated as β-heat treated alloy 5.

3.2.2 Autoclaving:

For oxidation study five coupons from each heat treated condition of alloy 1 and alloy 2 were pickled according to ASTM G2 for autoclave testing. Accelerated Autoclaving at 415° C, 10.3 MPa pressure for three days period [3.3] was done to observe the oxidation behavior of the differently heat treated alloy. The weight before and after accelerated autoclaving of the coupons
was taken on a balance of 0.01 mg accuracy and dimensions were measured with 0.05 mm accuracy as specified by ASTM G2.

Autoclaving of few samples was carried out at 500°C 10.3 MPa for 3 days to simulate nodular corrosion observed in boiling water environment of nuclear reactor.

For Zr-2.5Nb pressure tube material, three samples from each Fe level were taken and autoclaved oxide layer was removed by using emery paper. After that these samples were also pickled and following which autoclaving at 415° C, 10.3 MPa pressure for 3 days period was carried out. The weights before and after accelerated autoclaving of the coupons were measured. The thicknesses of the oxide layers formed on the samples as a result of autoclaving was determined by SEM.

3.2.3 H pick up measurement:

To measure hydrogen pick up during autoclaving, as received samples and samples after accelerated autoclaving were cut using a cut-off wheel and carbon tetrachloride as coolant. The autoclaved oxide layer was removed by dry grinding on coarse emery paper. After that the samples were cleaned in tetrachloride solution, dried and weighed. H content was determined using inert gas fusion technique [3.4]. Hydrogen measurement of standard Ti samples having H 16±2ppm and 27±2ppm respectively was done before and after testing of each coupon. The microstructures of the autoclaved samples were also examined to establish if hydrides had formed.

3.2.4 Optical Microscopy:

For optical microscopy work, samples of Zr-Sn-Fe-Cr series were polished mechanically and then chemically in 45 % HNO₃-45% H₂O-10% HF solution.

3.2.5 Scanning Electron Microscopy:
Specimens for scanning electron microscopy (Camscan CS3200L) were prepared by mechanical grinding and subsequent etching in a glycerine: Hf : HNO₃ (6 : 2 :1) solution for nearly 20 sec to reveal second phase particles in Zr-Sn-Fe-Cr alloys. For Zr-Nb series alloys, samples were prepared by mechanical grinding and subsequent etching in HF : HCl : HNO₃ (2 : 2:1) solution to reveal the second phases.

3.2.6 Transmission Electron Microscopy:
For transmission electron microscopy, 100 µm thick discs with 3 mm diameter were made and electro polished in a solution of 20% perchloric acid and 80% methanol at -50° C using jet-thinning apparatus. These electron transparent foils were examined at 160KV using JEOL transmission electron microscope. Elemental analyses were performed using an energy dispersive spectrometer (EDS) attached with STEM.

3.2.7 Cross sectional TEM sample preparation technique:
For observation of oxide in the cross section, samples with small transverse cross-sections of tubing that were prepared according to the following procedure. Two samples having axial segments of about 1.5 mm width and 10 mm height were cut from the autoclaved oxidized Zr-2.5Nb pressure tube material and oxidized Zr-Sn-Fe-Cr alloys. Then the two pieces were glued together such a way that the oxide surfaces were facing each other. Then this joined piece was inserted into a slot having width 1.1mm and is made on 2.5 mm (diameter) x 12mm (height) Mo rod. Then the whole assembly was placed inside a brass tube having outer diameter 3mm and inner diameter 2.5mm. This attachment was bonded in place using Devcon (R) epoxy resin with hardener. Slices about 0.5 mm thick were then cut from the brass tube to provide 3 mm diameter disks with the oxide cross-section located near the center of the disk. The disk samples were ground on 600 grit silicon carbide paper on both sides until the thickness was approximately 100 µm. These disks were then dimpled by using dimple grinder with the dimple centered near the oxide–oxide interface. The dimple was made by using progressively finer diamond abrasives followed by a final polish using 0.05 µm alumina. Dimples were made on both sides of the disk with the final thickness of the disk at the bottom of the dimple is around 40 µm. After that GATAN ion milling at 4.3 kV was carried out for sufficient time such that electron should
transmit through the oxide. Throughout the sample preparation and polishing, care was constantly exercised to avoid sample deformation and to remove the damaged oxide from the cutting operation because of the sensitivity of the oxide to develop lateral cracks during preparation.

Fig. 3. 2 Steps involved in making cross sectional sample (diagram not in scale).
3.2.8 Micro-hardness measurement:

Vickers hardness measurements using 300 gm load with 10 s dwelling time were carried out on all the annealed samples heat treated at two different temperatures for various lengths of time. For Zr-2.5Nb pressure tube material with different Fe content, Vickers hardness measurements were carried out in a plane containing longitudinal-transverse directions. Eleven measurements on each samples were done to get the hardness of the alloys.

3.2.9 Small Angle Neutron Scattering (SANS):

Small angle scattering (SAS) is a powerful nondestructive technique to investigate structural features (size or size distribution, shape, inter-particle spacing) of the in-homogeneities (second phase precipitates or particles or pores in porous medium) or the density fluctuations in condensed matter [3.5, 3.6], on a length scale ranging from one nanometer up to one micron in a large specimen without any special sample preparation. Small angle scattering refers to the scattering at small wave vector transfer and is caused by the variation of scattering length density over a distance exceeding the normal inter-atomic distances in condensed systems. SAS differs from Bragg or diffuse scattering in the sense that it refers to scattering at small magnitude of wave vector transfer compared to the smallest reciprocal lattice vector in crystalline material or to that first maximum of the structure factor in non crystalline materials. So study of gross scale structural properties of a medium overlooking the specific details over inter-atomic distances is possible. Generally X-ray or neutrons are used as incident radiation for SAS investigations and the techniques are named as Small angle X-ray scattering (SAXS) or Small angle neutron scattering (SANS) respectively. In SAXS, as X-rays get scattered by electrons, it investigates inhomogeneities in electron density whereas SANS probes inhomogeneities in nuclear scattering length density. It is worthy to mention that SANS [3.7] is an useful nondestructive tool to obtain statistically averaged morphological information about inhomogeneities that are present in an alloy. It is to be mentioned that SANS and TEM are complementary in nature. TEM provides direct information on localized zone while SANS gives statistically averaged information from bulk.
SANS measurements were carried out to find the size and distribution of second phase precipitates in Zr-Sn-Fe-Cr series alloy in a thick specimen to get good statistical averaged information and have been performed using a double crystal based medium resolution small-angle neutron scattering instrument (MSANS) [3.7] at the guide tube laboratory of DHARUVA reactor, India. The scattered intensities [I(q)] have been recorded as a function of wave vector transfer function \( q = \frac{4\pi\sin(\theta)}{\lambda} \), where 2\( \theta \) is the scattering angle and \( \lambda \) (= 0.312 nm.) is the incident neutron wavelength for the present experiment. The specimens (~2 mm) were placed on a sample holder with a circular slot of 1.5 cm diameter. The SANS data were corrected for background, transmission and instrument resolution effects [3.8].

3.2.10 X-ray photo Electron Spectroscopy:

X-ray photo-electron spectroscopy (XPS) [3.9] is a surface sensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand range, chemical state and electronic state of the elements that exist within material. The XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and the number of photo electrons that escape from the top 0 to 10 nm of the surface. Very high vacuum or ultra vacuum is required. Fig.3.3 depicts the principles of XPS technique. A typical XPS spectrum is a plot of the number of electrons detected versus binding energy of the electrons detected. The binding energy of the electron can be determined by using an equation that is based on the work of Ernest Rutherford [3.10].

\[
E_{binding} = E_{Photon} - (E_{Kinetic} + w_{p}) - - - - - 3.2
\]

where \( E_{binding} \) is the binding energy (BE) of the electron, \( E_{Photon} \) is the energy of the X-ray photon being used, \( E_{Kinetic} \) is the kinetic energy of the electron as measured by the instrument and \( w_{p} \) is the work function of the spectrometer.

Each element produces a characteristic set of XPS peaks at characteristic binding energy that directly identify each element present in or on the surface of the material analyzed. These characteristic spectral peaks correspond to the electron configuration of the electrons within the
atoms, e.g., 1s, 2s, 2p, 3s, etc. The number of detected electrons in each of the characteristic 
peaks is directly related to the amount of element within the XPS sampling volume. To generate 
atomic percentage values, each raw XPS signal must be corrected by dividing its signal intensity 
(number of electrons detected) by a "relative sensitivity factor" (RSF), and normalized over all of 
the elements detected. Since hydrogen is not detected, these atomic percentages exclude 
hydrogen. This technique is also called as Electron spectroscopy for chemical analysis (ESCA).

To establish the chemical state of elements in the oxide film, the outermost surface of all the 
alloys were analyzed with XPS using hemispherical Thermo VG Clam2 analyzer. Detailed scans 
of C 1S, Zr 3d, Nb 3d, Fe, O 1S were obtained with monochromatic Mg Kα X-ray source. The 
area of analysis was approximately 100 mm². The binding energy of O1s, Zr 3d and Nb 3d was corrected 
taking C 1S peak at 284.5 ev.

3.2.11 Grazing Incidence X-ray Diffraction (GIXRD):

Grazing Incidence X-ray diffraction technique is used to record the diffraction pattern of thin 
films, with minimum contribution from substrate. It is a nondestructive surface sensitive
technique. Since the angle of incidence (α) of X-ray beam decreases, so that the refractive index is less than unity, total external reflection of X-rays occurs below critical angle of incidence αc. The diffracted and scattered signals at the angle 2θ arise only from the limited depth from surface depending upon angle of incidence. While the detected signal is Bragg-diffracted at a lattice plane directed perpendicular to the surface, the method possesses the capabilities of measuring residual stress or phase analysis across the depth. The experimental set up for carrying out GIXRD is shown in fig.3.4. GIXRD was performed using a rotating anode X-ray diffractometer with Cu Kα radiation in order to obtain information about the oxide structure from the specimens so that the normal direction to their surface corresponded to the radial direction of the pressure tube. The grazing incident angles of 0.5°, 1°, 5° and 10° were used to study the oxide structure along the thickness direction.

![Grazing Incidence X-ray Diffraction principle](image)

**Fig. 3.4 Schematic Diagram of Grazing Incidence X-ray Diffraction principle where parallel monochromatic X-ray beam falls on a sample surface at a fixed angle of incidence (α) so that signal comes mostly from the oxide film, not from substrate and the diffraction profile is recorded by detector (internet source).**

The linear absorption coefficient (μ) of ZrO₂ oxide is 581.84 cm⁻¹ [3. 11] and for Zr it is 898.46 cm⁻¹. The depth of penetration (τ) was calculated using the following relationship at 0.5°, 1°, 5° and 10° and are given in table 3.4.

\[ \tau = \frac{\sin \alpha}{\mu} \]

\[ \tau = -3.3 \]
Table 3.4: Depth of penetration at different grazing angle in Zr metal and its oxide

<table>
<thead>
<tr>
<th>Grazing angle (α)</th>
<th>Depth of penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZrO₂(nm)</td>
</tr>
<tr>
<td>0.5°</td>
<td>150</td>
</tr>
<tr>
<td>1°</td>
<td>300</td>
</tr>
<tr>
<td>5°</td>
<td>1498</td>
</tr>
<tr>
<td>10°</td>
<td>2984</td>
</tr>
</tbody>
</table>

3.2.12 Ion and neutron Irradiation:

The oxide surface of the Zr-2.5Nb alloy and alpha annealed (700°C for 10 hrs.) Zr-Sn-Fe-Cr alloys were irradiated with 306 KeV Ar⁺⁹ ions at a dose of 3X10¹⁹ Ar⁺⁹ /m². To compare the effect of heavy ion irradiation with proton irradiation, oxide surface of annealed (800°C for 10 hrs.) Zr-Sn-Fe-Cr alloy was irradiated with 3.5MeV proton using the beam at the Variable Energy Cyclotron Centre (VECC), Calcutta, at dose of 5x10²⁰ proton/m². The samples for irradiation were mounted in a target holder flange, made of aluminum. The dose accumulating to the target material (sample) was measured from the total charge of projectile particles i.e. protons falling on the sample. Water is allowed to flow to the target flange to minimize the heat generated during irradiation. The temperature did not rise above 313 K, as monitored by a thermocouple sensor placed inside a groove of the flange in close proximity to the sample [3.12]. The displacements per atom (dpa) in both the case was obtained using TRIM programme. The irradiated oxides were characterized using GIXRD and XPS technique.

The fuel tube which was irradiated upto 7600MWD/T burn up was received. After decladding, a slice of 2 mm x 5 mm was made and inner side was ground to move the fuel contamination. During sample preparation proper care was taken so that no damage occurred in the outer surface of the tube. After ultrasonic cleaning it was taken out for GIXRD study.

3.2.13 Computational technique:

For prediction of microstructure evolution during diffusion controlled phase transformation in Zr-Nb substitutional alloy system, phase field technique has been adapted. This phase field
technique which is based on diffuse interface concept, features large scale separation. The interface is of the order of nanometers while characteristic features of microstructure present on a scale of micrometers. This scale separation can pose main computational drawback often preventing results to be quantitative. This problem can be overcome by using adaptive meshing as the variations of the phase field and diffusion fields are localized over the interfacial region. This adaptive grid would follow the migration of the phase boundary and give high accuracy. Adaptive Finite Element method in combination with the phase field model has been used to simulate diffusional phase transformation in Zr-Nb alloy system.

3.3 References:


3.2 Waterside corrosion of zirconium alloys in nuclear power plants, IAEA TECHDOC- 996, 124-169.


3.4 Dennis Lawrenz, John Hawkinswww.leco.com/resources/application.../O-N%20209-141-003.pdf.


