List of Figures

Fig. 2. 1  Zr-O phase diagram at 1 bar pressure [2. 5].  8
Fig. 2. 2  Pressure-Temperature diagram of ZrO$_2$ [2. 7].  9
Fig. 2. 3  The typical cracked white oxide forms in pure Zr after 415° C 1500 psi 72 hrs.
exposure in author’s lab.  10
Fig. 2. 4  Binary Zr-Sn phase diagram [2. 15].  13
Fig. 2. 5  Binary Zr-Fe phase diagram [2. 15].  14
Fig. 2. 6  Binary Zr-Cr phase diagram [2. 15].  14
Fig. 2. 7  Binary Zr-Ni phase diagram [2.15].  15
Fig. 2. 8  Binary Zr-Cu phase diagram [2. 15].  18
Fig. 2. 9  Schematic diagram of weight gain of different Zr alloys with exposure time for
different oxidation regime.  22
Fig. 2. 10  Relation between weight gains on single crystals of van Arkel Zirconium (after
1min at 500 °C 1 atm. pressure with different crystal orientations [2. 30].  22
Fig. 2. 11a  Nodules formed in the fuel clad during exposure in BWR [2.75] [Internal report,
PIED, BARC].  26
Fig. 2. 11b  Nodules formed in the fuel clad during 500°C autoclaving at 10.3 MPa pressure
27
Fig. 2. 11c  Cross sectional view of lenticular shape of the nodules formed in the fuel clad
during 500°C autoclaving at 10.3 MPa pressure.  27
Fig. 2. 11d  Enlarge view of lenticular shape of the nodules showed presence of cracks parallel
to metal oxide interface.  28
Fig. 2. 12  A schematic showing the steps leading to the nucleation of nodular oxide on
Zircaloy fuel sheath in reactor.  28
Fig. 2. 13  Correlation between relative corrosion rates to the mean diameter (µm) of second
phase particles in Zircaloy fuel sheath in reactor [2. 34].  30
Fig. 2. 14  Binary Zr-H phase diagram [2. 5].  32
Fig. 3. 1  Fabrication flow sheet for production of seamless Zr-2.5%Nb pressure tubes for
PHWR at NFC, Hyderabad [3.1].  50
Fig. 3. 2  Steps involved in making cross sectional sample (diagram not in scale).  55
Fig. 3. 3  Schematic Diagram of principles of X-ray photoelectron spectroscopy technique
where probing beam is Al X-ray having 1486 eV energy (Internet Source).  58
Fig. 3. 4  Schematic Diagram of Grazing Incidence X ray Diffraction principles 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).  59
Zr-Nb phase diagram. The points A, B, D, E and F specify the operating points i.e. the alloys with corresponding simulating temperature for Widmanstatten plates and C for planar growth respectively.

Typical grain boundary $\alpha$ Allotrimorph observed surrounding the prior $\beta$ grain along with lath shaped product formed in Zr-Nb alloy during cooling from $\beta$ phase [4.62].

Typical Widmanstatten lath found in Zr-2.5Nb alloy during gas quenching from $\alpha + \beta$ phase [6.63].

Variation of the function $p(\varphi)$ w.r.t $\varphi$ is plotted.

Variation of the function $q(\varphi)$ w.r.t $\varphi$ is plotted.

Adaptive meshing where the interface regions have been discretized using five grid points and the rest of the region with large triangles.

Effect of $\gamma$ parameter on the side plate-lengthening rate.

Effect of $\gamma$ parameter on the side plate-widening rate.

More or less uniform distribution of concentration field (mole fraction of Nb) across the entire interface leads to planar growth. The domain size is 3.88 $\mu$m x 1.5 $\mu$m.

Distribution of concentration field (mole fraction of Nb) during lath formation. Movement of planar interface is restricted due to solute accumulation and growth of tip leads to lath formation. The domain size is 3.88 $\mu$m x 1.5 $\mu$m.

Distribution of phase field variable (phi) during lath formation. The domain size is 3.88 $\mu$m x 1.5 $\mu$m.

Distribution of concentration field (mole fraction of Nb) during growth of multiple lath from allotrimorph $\alpha$ at 890 K. The domain size is 3.5 $\mu$m x 1.5 $\mu$m.

(a) Distribution of concentration field (mole fraction of Nb) in initial microstructure having various size of protrusions of grain boundary $\alpha$ in a matrix of $\beta$,

(b) Evolution of microstructure during growth of grain boundary $\alpha$ at 890 K. The domain size is 3.28 $\mu$m x 1.5 $\mu$m.

Distribution of concentration field (mole fraction of Nb) during development of $\alpha$ phase of different morphology from the initial protrusions of grain-boundary $\alpha$, (a) lower temperature and (b) higher temperature lath morphology. The domain size is 2.4 $\mu$m x 1 $\mu$m.

Distribution of concentration field (mole fraction of Nb) during development of allotrimorphs $\alpha$ from the protrusions of grain boundary $\alpha$ at 1095 K. The black line denotes the initial position of the interface. The domain size is 2.80 $\mu$m x 1 $\mu$m.

Development of Widmanstatten lath morphology from planar front of allotriomorph $\alpha$- Zr in Zr-2.5Nb alloy using implicit nucleation. Fig. 4.14a is the
initial microstructure. The dark region in fig. 4. 14a indicates pre-nucleated allotriomorph \( \alpha \)-Zr (\( \varphi = 0 \)). \( \varphi = 1 \) in the region of \( \beta \)-Zr. Fig. 4.14b, 4.14c, 4.14d are microstructure at different non-dimensional time steps (0.035, 0.0531, 0.0663 respectively). Planar front becomes unstable at 890 K. The colour code depicts the mole fraction of Nb in Zr-Nb binary alloy. The domain size is 1.57 \( \mu \text{m} \times 5.14 \mu \text{m} \).

Black line denotes initial position of the interface.

**Fig. 4. 15** Tip velocity as a function of undercooling in terms of \( (1/T) \) multiplied by 1000. Lower temperature i.e. higher undercooling favoured Widmanstatten lath morphology.

**Fig. 4. 16** Stable planar front grows from pre-nucleated allotriomorph \( \alpha \)-Zr of Zr-2.5Nb alloy at 1054 K. No stable perturbation has been formed at this temperature. The dark region in 16a indicates pre-nucleated allotriomorph \( \alpha \)-Zr. The images (fig. 4. 16a and fig. 4. 16b) were taken at 0.0, 0.107 non-dimensional time steps. The colour code depicts the mole fraction of Nb in Zr-Nb binary alloy. Black line in fig. 4. 16b denotes initial position of the interface. The domain size is 1.57 \( \mu \text{m} \times 5.08 \mu \text{m} \).

**Fig. 4. 17** Development of Widmanstatten lath morphology at 890 K from allotriomorph \( \alpha \)-Zr in Zr-2.5Nb alloy using explicit nucleation. 17a is the initial microstructure and 17b is the microstructure at 0.0814 non-dimensional time step. The grayscale colour code depicts the mole fraction of Nb in Zr-Nb binary alloy. The domain size is 1.8 \( \mu \text{m} \times 4.26 \mu \text{m} \).

**Fig. 4. 18** Position of interface at different instant (dimensionless) for Widmanstatten plate growth at 890 K indicate linear lengthening rate.

**Fig. 4. 19** Position of interface at different instant (dimensionless) for diffusion controlled planar growth at 1054 K. Interface position was taken the location where \( \varphi = 0.5 \) at different instant.

**Fig. 4. 20** Tip velocity as a function of supersaturation \( \Omega_0 \) at 890 K. At very high supersaturation steeper slope presents and transition was observed at \( \Omega_0 0.83 \).

**Fig. 4. 21** Contour plot of \( \varphi = 0.5 \) showing interface position at different instant. For Zirconium with less than 200 ppm Nb, lath morphology does not develop and initial protrusions decay and a planar interface formation is favored with very high value of \( \gamma \) (120).

**Fig. 5. 1** Basket weave microstructure of as received triple arc melted ingot of Zr-1.53 Sn-Fe-Cr alloy.

**Fig. 5. 2** Cold worked and quenched microstructure of Zr-1.53Sn-Fe-Cr alloy, a) Basket weave microstructure observed in optical microscope, b) TEM microstructure of single lath.

**Fig. 5. 3** Optical micrograph of alloy 1 annealed at 700°C for a) 15 minutes, b) 1hr. and c)
Fig. 5.4  SEM micrograph alloy 1 annealed at 700°C for a) 15 minutes, b) 1hr. and c) 10 hrs.

Fig. 5.5  a) TEM micrographs showing both grain body and grain boundary precipitates, size distribution of b) globular precipitates and c) smaller side of parallelepiped precipitates (with aspect ratio around 2.5) after annealing at 700°C for 1 hr. The number of particles analyzed is given as N.

Fig. 5.6  a) TEM micrographs showing both grain body and grain boundary precipitates, b) size distribution of globular precipitates and c) smaller side of parallelepiped precipitates (with aspect ratio around 3.5) after annealing at 700°C for 10 hrs.

Fig. 5.7a EDS profile of matrix shows presence of Sn after annealing at 700°C for 10 hrs.

Fig. 5.7b Zr-Sn rich parallelepiped precipitates were seen to strain the matrix.

Fig. 5.7c EDS profile (5.7c - 2) at larger precipitates (5.7c-1) indicates it is Zr lean, Zr(FeCr)_2 type.

Fig. 5.7d EDS profile (5.7d-2) of precipitates (5.7d-1) with aspect ratio one indicates it is Zr rich, Zr_2(FeCr) type.

Fig. 5.8  a) TEM micrographs showing both grain body and grain boundary precipitates in alloy 2 after annealing at 800°C for 1 hr. with b) Distribution of globular precipitate and c) Distribution of parallelepiped precipitates (smaller side and aspect ratio 2 to 5).

Fig. 5.9  a) Distribution of globular precipitate in alloy 2 after annealing at 800°C for 10 hrs and b) Distribution of smaller side of parallelepiped precipitates (with aspect ratio around 2.5) in alloy 2 after annealing at 800°C for 10 hrs.

Fig. 5.10a Variation of hardness with annealing time in Vicker’s Scale using 300 gm load in alloy-1.

Fig. 5.10b Variation of hardness with annealing time in Vicker’s Scale using 300 gm load in alloy-2.

Fig. 5.11a Scattered points showing extracted SANS profiles from various alpha annealed heat-treated samples. The solid line represents the fit of the model.

Fig. 5.11b Estimated size distributions of diameter of the precipitates present in different annealed conditions assuming spherical particle model.

Fig. 5.11c Estimated size distributions of smaller length scale parallelepiped precipitates present in different annealed conditions.

Fig. 5.11d Estimated size distributions of larger length scale parallelepiped precipitates present in different annealed conditions.

Fig. 5.12a Oxidation behavior of the alloy 1 (Zr-1.53Sn-TM) and alloy 2 (Zr-1.35Sn-TM) at 415°C 10.3 MPa for 3 days which were annealed at 700°C & 800°C for with different duration.
Fig. 5.12b  Oxidation behavior after autoclaving at 415° C 10.3 MPa for 3 days of alloy 1(Zr-1.53Sn-TM) and alloy 2 (Zr-1.35Sn-TM) with different annealing conditions represented by CAP values.

Fig. 5.13a  0.5° grazing angle reflection from oxide of as quenched Zr-1.35Sn-TM alloy, shows reflection from monoclinic phase, hexagonal Zr$_3$O reflection and very small (101) tetragonal reflection.

Fig. 5.13b  1° grazing angle reflection from oxide of as quenched Zr-1.35Sn-TM alloy, shows reflection from monoclinic phase, (101) hexagonal Zr$_3$O reflection.

Fig. 5.13c  5° grazing angle reflection from oxide of as quenched Zr-1.35Sn-TM, shows majority of reflection from matrix α-Zr along with oxide.

Fig. 5.13d  1° grazing angle reflection from oxide of as quenched Zr-1.5Sn-TM alloy, shows majority of reflection from matrix α-Zr along with monoclinic and tetragonal reflection.

Fig. 5.13e  0.5° grazing angle reflection from oxide of Zr-1.5 Sn-TM alloy in 700°C/15 mins. annealed condition, shows majority of reflection from monoclinic and reflection from Zr$_3$O was found.

Fig. 5.13f  5° grazing angle reflection from oxide of Zr-1.5 Sn-TM alloy in 700°C/15 mins. annealed condition, shows majority of reflection from matrix α-Zr along with monoclinic and tetragonal reflection.

Fig. 5.13g  10° grazing angle reflection from black oxide of fuel tube formed at 500°C autoclaving, shows majority of reflection from monoclinic ZrO$_2$ oxide.

Fig. 5.14a  Intensity of XPS lines spectra of the oxide formed during autoclaving at 415°C on α-annealed (700°C/1h.) Zr-1.3Sn-TM alloy showing Zr 3d5/2 binding energy peak at 182.1 eV. No 3d peak of Sn was found.

Fig. 5.14b  Intensity of XPS lines spectra of the white nodular oxide formed during autoclaving at 500°C on Zircaloy-4 fuel tube showing Sn 3d5/2 binding energy peak at 485.9 eV.

Fig. 5.14c  Intensity of XPS lines spectra of the black oxide formed during autoclaving at 500°C on inner side of Zircaloy-4 fuel tube showing Sn 3d5/2 binding energy peak at 486.1 eV.

Fig. 5.15  a. Bright field TEM image of oxide in cross sectional sample, b. Dark field TEM image of oxide in cross sectional sample indicating columnar grains, c. Selected area diffraction pattern of oxide near oxide metal interface indicates presence of nanocrystalline grains.

Fig. 6.1a  Transmission electron micrographs Zr-2.5Nb pressure tube material in alloy 3, showing elongated α-Zr grains surrounded by β-phase.

Fig. 6.1b  Bright field transmission electron micrographs of Zr-2.5Nb pressure tube material
in alloy 3, showing discontinuous $\beta$ at $\alpha$-$\alpha$ grain boundary as well as within $\alpha$ grain.

Fig. 6. 1c Discontinuous globular as well as stringer shape $\beta$-phase at $\alpha$-$\alpha$ grain boundary in alloy 3.

Fig. 6. 1d EDS scan of $\beta$ phase present at grain boundary in alloy 3.

Fig. 6. 2a Microstructure of Zr-2.5Nb pressure tube material in alloy 4, showing stringer form $\beta$ phase and discontinuous $\beta$ particles at $\alpha$/a boundary and $\beta$ particles within $\alpha$ grain.

Fig. 6. 2b Enlarged view of grain boundary $\beta$ phase particles in alloy 4.

Fig. 6. 2c Fe, Nb and Zr bearing parallelepiped precipitates in alloy 4.

Fig. 6. 2d EDS scan shows Fe enrichment in the precipitates in alloy 4.

Fig. 6. 3a: Bright field TEM micrograph of alloy 5, showing lamellar structure.

Fig. 6. 3b Dark field TEM micrograph of alloy 5, showing elongated $\alpha$-Zr grains surrounded by discontinuous $\beta$-phase.

Fig. 6. 3c EDS profile of Zr rich grain boundary $\beta$.

Fig. 6. 3d Dark field TEM micrographs of globular grain body $\beta$ phase.

Fig. 6. 3e EDS profile of Nb rich grain body $\beta$ phase in alloy 5.

Fig. 6. 3f Dark field TEM micrographs of scattered Zr-Fe rich grain body precipitates in alloy 5.

Fig. 6. 3g Backscattered SEM image shows of higher fraction of $\beta$-phase $\alpha$-matrix of heat-treated alloy-5.

Fig. 6. 4 Relationship between Fe content in Zr-2.5Nb alloy and weight gain after 415°C, 10.3MPa, 3 days steam autoclave testing showing beneficial effect of Fe in improving oxidation resistance.

Fig. 6. 5a Relationship between Fe content in Zr-2.5Nb alloy with Hydrogen pick up during 415°C, 10.3MPa, 3 days steam autoclave testing showing detrimental effect of Fe in H intake.

Fig. 6. 5b Hydrides were observed under SEM in alloy 5 after 72 hrs. autoclaving at 415°C.

Fig. 6. 6a Floppy and cracked oxides with its wavy interface observed under SEM in alloy 3 after 72 hrs. autoclaving at 415°C, fig. 6. 6b: Enlarged View of the oxide.

Fig. 6. 7 Cracks or pore free oxide and its wavy interface observed under SEM in alloy 4 after 72 hrs. autoclaving at 415°C.

Fig. 6. 8a Dense oxide and its wavy interface observed under SEM in alloy 5 after 72 hrs. autoclaving at 415°C.

Fig. 6. 8b Floppy and porous oxides with its wavy interface observed under SEM in heat-treated alloy 5 after 72 hrs. autoclaving at 415°C.

Fig. 6. 8c Enlarged View of the oxide.
Fig. 6. 8d The oxide surface observed under SEM in heat-treated alloy 5 after 72 hrs. autoclaving at 415°C.

Fig. 6. 9a XPS spectra of the oxidized Zr-2.5Nb with 1200 ppm Fe after exposure to accelerated steam at 415°C.

Fig. 6. 9b Intensity of XPS lines in Zr 3d spectra of the oxidized Zr-2.5Nb with different content of Fe after exposure to accelerated steam showing Zr 3d5/2 binding energy peak for all the alloy in within 181.9-182.2 eV.

Fig. 6. 9c Intensity of XPS lines in O 1S spectra of the oxide of Zr-2.5Nb with different content of Fe after exposure to accelerated steam, showing 1s oxygen peak of Zr at 530.6 eV and the other 1s oxygen for Nb was at 528.6 eV indicating presence of both the oxide.

Fig. 6. 9d Intensity of XPS lines in Nb 3d spectra of the oxidized Zr-2.5Nb with different content of Fe after exposure to accelerated steam showing Nb 3d5/2 binding energy peak for all the alloys in within 206.7 - 206.9 eV.

Fig. 6. 9e Well-resolved doublet of Zr 3d spectra of the oxidized heat-treated Zr-2.5Nb observed after exposure to accelerated steam showing Zr 3d5/2 binding energy peak at 181.79 eV.

Fig. 6. 9f Intensity of XPS lines in O 1S spectra of the oxide of heat-treated Zr-2.5Nb after exposure to accelerated steam, showing only 1s oxygen peak of Zr at 530.6 eV.

Fig. 6. 10a GIXRD scan of the oxide at 1 degree incidence angle in alloy 3 after exposure to accelerated steam at 415°C showing presence of small fraction of tetragonal Zirconia along with monoclinic structure of oxide.

Fig. 6. 10b GIXRD scan on the oxide 1 degree incidence angle in alloy 4 after exposure to accelerated steam at 415°C showing presence of relatively higher fraction of tetragonal Zirconia along with monoclinic structure of oxide.

Fig. 6. 10c GIXRD scan on the oxide showing presence of tetragonal Zirconia along with monoclinic structure of oxide as well as α-Zr peaks with increasing grazing angle of incidence alloy 4 after exposure to accelerated steam at 415°C.

Fig. 6. 10d The negative slope of β cos(θ) vs. sin(θ) indicated presence of compressive stress in oxide at a 0.5° grazing angle incidence in case of alloy 4.

Fig. 6. 10e,f e. Dark field TEM image of oxide in cross sectional sample indicating columnar grains, f. Selected area diffraction pattern of oxide indicates presence of nanocrystalline textured grains.

Fig. 6. 10g GIXRD scan on the oxide showing presence of significant tetragonal Zirconia along with monoclinic structure of oxide as well as Zr3O peak at 0.5° grazing angle of incidence heat treated alloy after exposure to accelerated steam at 415°C.

Fig. 6. 10h GIXRD scan on the oxide showing presence of significant tetragonal Zirconia
along with monoclinic structure of oxide as well as Zr$_3$O peak at 5° grazing angle of incidence heat treated alloy after exposure to accelerated steam at 415°C.

Fig. 7.1 (a) Damage profile of 306KeV Ar$^{19}$ ions in oxide of Zirconium calculated by SRIM-2008. (b) Plot showing the range of ions (193 nm) in target, whereas oxide is having thickness 1200 nm.

Fig. 7.2 (a) Damage profile of 3.5MeV proton ions in oxide of Zirconium calculated by SRIM-2008. (b) Plot showing the range of ions (69.4 µm) in target, whereas oxide is having thickness 1200 nm.

Fig. 7.3a Before Irradiation, 0.5° grazing angle reflection shows mostly reflection from monoclinic phase.

Fig. 7.3b Before Irradiation 1° grazing angle reflection shows mostly reflection from monoclinic phase.

Fig. 7.3c Before Irradiation 5° grazing angle reflection shows reflection from tetragonal, monoclinic oxide and α-Zr phase.

Fig. 7.3d Before Irradiation 10° grazing angle reflection from oxide metal interface of Zr-2.5Nb alloy shows reflection of mostly α-Zr phase and monoclinic oxide phase.

Fig. 7.4a After Ar Irradiation 0.5° grazing angle reflection from oxide of Zr-2.5Nb alloy shows significant tetragonal reflection. Reflection intensity from monoclinic phases reduces.

Fig. 7.4b After Ar Irradiation 1° grazing angle reflection shows significant tetragonal reflection. Reflection intensity from monoclinic phases reduces.

Fig. 7.4c After Ar Irradiation 5° grazing angle reflection shows reflection from tetragonal, monoclinic oxide and α-Zr phase.

Fig. 7.4d After Irradiation 10° grazing angle reflection shows reflection from mostly α-Zr phase and monoclinic oxide phase. Tetragonal reflection at 30.24° is also found.

Fig. 7.5a Before Irradiation 0.5° grazing angle reflection shows reflection from monoclinic phase.

Fig. 7.5b Before Irradiation 1° grazing angle reflection shows mostly reflection from monoclinic phase.

Fig. 7.5c Before Irradiation 5° grazing angle reflection shows reflection from tetragonal, monoclinic oxide and α-Zr phase.

Fig. 7.5d Before Irradiation 10° grazing angle reflection from oxide metal interface of Zr-Sn-Fe-Cr alloy shows reflection from mostly α-Zr phase and monoclinic oxide phase.

Fig. 7.6a After Ar Irradiation, 0.5° grazing angle reflection from oxide of Zr-Sn-Fe-Cr alloy shows significant tetragonal reflection. 100% intensity in peak was shifted to an angle where both tetragonal and monoclinic peaks present.

Fig. 7.6b After Ar Irradiation 1° grazing angle reflection shows significant tetragonal
reflection.

Fig. 7. 6c After Ar Irradiation 5° grazing angle reflection shows reflection from tetragonal, monoclinic oxide and α-Zr phase.

Fig. 7. 6d After Irradiation 10° grazing angle reflection shows reflection from mostly α-Zr phase and monoclinic oxide phase. Tetragonal reflection at 30.24° is also found.

Fig. 7. 7a Before Irradiation, 0.5° grazing angle reflection shows mostly reflection from monoclinic phase.

Fig. 7. 7b Before Irradiation 1° grazing angle reflection shows mostly reflection from monoclinic phase with very small fraction of tetragonal reflection.

Fig. 7. 7c Before Irradiation 5° grazing angle reflection shows reflection from tetragonal, monoclinic oxide and α-Zr phase.

Fig. 7. 7d Before Irradiation 10° grazing angle reflection shows reflection from mostly α-Zr phase and monoclinic oxide and small amount of tetragonal oxide.

Fig. 7. 8a After proton Irradiation, 0.5° grazing angle reflection shows no tetragonal reflection. Reflection intensity is only from monoclinic phases.

Fig. 7. 8b After proton Irradiation 1° grazing angle reflection shows no change in tetragonal reflection.

Fig. 7. 8c After proton Irradiation 5° grazing angle reflection shows reflection from tetragonal, monoclinic oxide and α-Zr phase.

Fig. 7. 8d After proton Irradiation 10° grazing angle reflection shows reflection from mostly α-Zr phase and monoclinic oxide and small amount of tetragonal oxide.

Fig. 7. 9a Oxide layer formed in reactor on the outer surface of the fuel clad. Oxide thickness 2.9-3.5 μm.

Fig. 7. 9b 0.5° grazing angle reflection shows significant tetragonal reflection as well as reflection from Zr₂O along with monoclinic phase.

Fig. 7. 9c 1° grazing angle reflection shows significant tetragonal reflection as well as reflection from hexagonal Zr₃O along with monoclinic phase.

Fig. 7. 9d 2°grazing angle reflection shows significant tetragonal reflection along with monoclinic phase and reflection from hexagonal ZrO₃.

Fig. 7. 9e 5°grazing angle reflection shows significant tetragonal reflection along with monoclinic and matrix α Zr phase.

Fig. 7. 10 Intensity of XPS lines in Zr and Nb 3d spectra of heavy ion irradiated oxidized Zr-2.5Nb showing Zr 3d5/2 binding energy peak is at 182.2 eV and Nb 3d5/2 binding energy peaks are at 206.2 corresponds to NbO₂ and 206.8 eV corresponds to Nb₂O₅.