THE EVOLUTION OF MICROSTRUCTURE AND DEFORMATION STABILITY IN ZR-NB-FE (SN,O) ALLOYS UNDER NEUTRON IRRADIATION

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«By three methods we may learn wisdom: first, by reflection, which is noblest; second, by imitation, which is easiest; and third, by experience, which is the bitterest»

Confucius
INTRODUCTION

Zr alloys with Nb (Zr-1Nb, Zr-2.5Nb) or with Sn, Fe, Cr, Ni (Zry-2, -4) are widely used in LWR and demonstrate the unique combination of nuclear, tensile and corrosion properties at moderate burnups.

E635 (Zr-1Nb-1.2Sn-0.35Fe) alloy, inferior to E110 (Zr-1Nb) in uniform corrosion, is resistant to nodular corrosion (boiling coolant, O), stable to strain under stresses and irradiation, has high strength. It was first reported in 1971 in Geneva. 20 years ago Dr. A. Nikulina described it in her Kroll medal paper. Based on understanding of Fe, Nb and O impact on corrosion, creep, growth, a new trend of developing materials for high burnups combining the properties of E110 (alloying with Fe and O - improving strength) and E635 (decreasing Sn and Nb – improving corrosion resistance) has appeared, keeping their advantages.

New Zr-Nb-Fe-Sn-O system alloys - ZIRLO, NSF, NDA, MDA, HANA… were developed for the water chemistry of PWRs and BWRs.
Identification of the Laves phase \((L)\) \(\text{Zr(Nb,Fe)}_2\)

SPPs type and nature are determined by \(\beta\)-Zr phase composition (hot rolling, cold working and anneals)- manufacturing, alloy composition

Precipitates in the E635 alloy tubes were first identified using SAD - HCP, \(a=0.54\) nm, \(c=0.87\) nm and X-Ray EDS microanalysis of SPPs extracted onto a carbon replica - composition \(35\text{Zr}-35\text{Nb}-30\text{Fe} (\pm 2\ \text{at.\%})\)

An additional phase depleted in Nb - \(\text{(Zr,Nb)}_2\text{Fe}\) precipitates (T-phase) were identified. Crystal lattice FCC, \(a=1.21\) nm, composition–\(60\text{Zr}-10\text{Nb}-30\text{Fe}\ (\text{at.\%}).\)
Microstructure of the Zr-Nb-(Fe-Sn) alloys

R = (Fe/Fe + Nb)_{0.3} - a relative element content in SPPs. ≈ 0.3% - Nb in matrix.

E110 with (0.03-0.15)%Fe or E635 with lower 0.15%Fe -- β-Nb + Laves phase.
E635 with higher-(0.4-0.6)%Fe - deficient Nb -- Laves phase + (Zr,Nb)_{2}Fe

Zr-1Nb E110
R < 0.05 β-Nb

E635(M) 0.35Fe
R = 0.05-0.15
β-Nb + Laves phase

E635 0.65Fe
R > 0.45
Laves phase + (Zr,Nb)_{2}Fe
Phase transformations

Above \((\alpha/\alpha+\beta)-(L)\) Zr(Nb,Fe)_2 and \(\beta\)-Nb dissolve at 700-750\(^\circ\)C, instead them - \(\beta\)-Zr and \((T)\) (Zr,Nb)_2Fe – dissolve at 750-800\(^\circ\)C.

Temperature of the \(\beta\)-Zr \((\alpha\rightarrow\alpha+\beta)\) of Zr-Nb alloys - 600-610\(^\circ\)C

In high Fe alloys \(\beta\)-Zr formation is delayed due to \((Zr,Nb)_2Fe\) – up to 640-680\(^\circ\)C

\[
\begin{align*}
\alpha\text{-Zr} + \beta\text{-Zr} &\leftrightarrow \alpha\text{-Zr} + \beta\text{-Zr} + L + T & 600-630^\circ\text{C} \\
\alpha\text{-Zr} + \beta\text{-Zr} + T &\leftrightarrow \alpha\text{-Zr} + L & 650-700^\circ\text{C}
\end{align*}
\]
DEFORMATION STABILITY- high resistance to shape changes under neutron irradiation (GROWTH AND CREEP)

INFLUENCE OF Zr-Nb-Fe-Sn COMPOSITION ON IRRADIATION GROWTH

(BOR-60, $E \geq 0.1$ MeV, $5.3$ dpa = $1 \times 10^{26}$ n/m$^2$)

The most affecting factor in the IIG of RXA Zr-Nb-Fe-Sn alloys is the Fe content. E635 type alloys ($0.25-0.65$)%Fe, ($0.6-2$)%Nb, ($0.6-1.5$)%Sn- low growth even at $30$ dpa. At the Fe content reduced to $0.10-0.15$% - a breakaway growth starts.
INFLUENCE OF Zr-1Nb (Fe) COMPOSITION

Dose dependence of alloys with 0.01–0.24 %Fe shows the breakaway (15-20 dpa)
As the Fe content increases: the incubation period prolongs, IIG decreases.
Even (0.03 – 0.07) % Fe substantially reduces irradiation growth.
Above the Fe solubility limit the effect becomes weaker.
Different structure state shows different growth:

**Annealed** - low IIG at a high dose, a long incubation period - α-matrix composition. 
(α+β)-**Quenched** - a linear growth at low doses, then a saturation stage: α-Zr do not contain Fe and Nb- increased c-dislocation density, α'-Zr -oversaturated Fe, Nb, Sn. 

**β - Quenched** – growth is extremely low- the isotropic texture, relation $\varepsilon \sim (1-3f_L)$. 

**CW** - a linear growth with low rate; a higher degree of CW leads to higher IIG. 

**E635** - the longest incubation period (RXA) and the lowest rate (CW). 

α-matrix composition (Zr-1.2%Sn-0.3%Nb-<0.02%Fe) – important
IRRADIATION CREEP

The favourable effect of the Fe alloying of Zr-1Nb - in the creep resistance. Additives of Fe (0.03-0.24%) result in a significant reduction of strain.

Influence of Fe content in the Zr-1Nb-0.10O alloy on the irradiation creep (1.3x10^{26} \text{ n/m}^{-2}, 113 \text{ MPa})
The yield strength depends on Fe content and grows with its increasing (0.03-0.24%).

The substantial increase in $\sigma_{0.2}$ - from 0.01 to 0.07% Fe.

Then the strength grows to a less extent - the cause of strengthening is irradiation-induced supersaturation due to matrix enrichment by Fe from the Laves phase.
Microstructure evolution after irradiation

- **E110, β-Nb**
  - Unirradiated
  - 20 dpa irradiated
  - c-dislocations, β-Nb \(\rightarrow\) less Nb, IIP

- **E110M, β-Nb+L**
  - Unirradiated
  - 20 dpa irradiated
  - β-Nb \(\rightarrow\) «β-Nb»
  - β-Nb \(\rightarrow\) less Nb, IIP, fewer c-dislocations

- **E635,E635M, L**
  - Unirradiated
  - 20 dpa irradiated
  - L \(\rightarrow\) less Fe \(\rightarrow\) «β-Nb»
  - L \(\rightarrow\) «β-Nb», few c-dislocations
Irradiated Laves phase $L_2 \text{Zr(Nb,Fe)}_2$

HCP–Fe depleting, transformation to polycrystalline BCC ($\beta$-Nb type)

1 dpa 10 dpa 20 dpa

100 nm
Irradiation- Fe content in Laves phase and Nb content in β-Nb

Under irradiation Laves phase becomes depleted in Fe that oversaturates matrix – the solid solution strengthening of Zr-Nb-Fe-(Sn) alloys – E635, E110M. It was for the first time the change in composition under irradiation was quantified. At low fluences < (5-10) dpa some Fe depletion does not lead to a change of lattice (HCP), when a specific composition is reached - Laves phase transforms into a phase of the β-Nb type (BCC).
Irradiated T-phase \((\text{Zr,Nb})_2\text{Fe}\) Precipitates

\[ \text{damage dose - 20 dpa} \]

Plate precipitates at the periphery

Element distribution within particle and on boundary with matrix

Precipitates (FCC, 60Zr-10Nb-30Fe (at.%) seem not to experience any changes. However, later on the periphery depletion with Zr, Fe and formation of Nb-enriched particles were revealed.
Irradiation–induced precipitates (IIP)

E110

E110M (0.12% Fe)

E635 type alloys (Zr-Nb-Fe-Sn)

E110 VVER

Fine plate-like (ellipsoid shaped) particles \((4-10) \, \text{nm}\), alignment parallel to the basal planes in dependence on Nb, Fe, Sn and stress.

Zr-Nb-Fe-Sn–lower number density, size \((3-7) \, \text{nm}\) enriched in Nb and Fe?
DISLOCATION STRUCTURE

irradiated E110 (without Sn and Fe)

c-type, $g=0002$

nonalignment of a-type loops, $g=10.1$

irradiated E635 type alloy

c-type dislocations close to SPP, few $g=0002$
a-type loops alignment, $g=10.1$
E110 alloy cladding tubes - in VVER
(burnup 54 MW·day/kgU – 20 dpa)

fine IIP precipitates enriched in Nb, precipitates of β-Nb and c-component dislocations

A neutron irradiation -redistribution of Fe and Nb between the α-solid solution and SPPs, alter the anisotropy of the diffusion of vacancies/interstitials, influence the separation of defect flows and formation of c-component vacancy loops and IIPs.
SUMMARY

The regularities in the Zr-Nb-(Fe-Sn) alloys microstructure evolution under neutron irradiation and the shape changes were established. It allowed to predict the alloys in-pile behaviour and recommend the trend and alloy compositions for high burnups.

Modification of E110 alloy - Improving strength, irradiation growth and creep resistance alloying with Fe and O - an increase of Fe in the matrix under neutron irradiation, thus hardening the alloy

E110M – Zr - 1Nb - 0.12Fe - 0.13O

Modification of E635 alloy - High resistance to uniform corrosion by decreasing the content of tin and niobium, high resistance to creep and growth:

E635M - Zr- 0.8Nb - 0.3 Fe - 0.8Sn - 0.09O

The weak dependence on fluence, low c-dislocations density, low growth strain (≤0.2 % at 20 dpa)– the composition of alloy and

α-matrix Zr-1.2 Sn-0.3 Nb-<0.05 Fe.

The Nb and Fe content the most favourable for irradiation growth, corrosion resistance and strengthening - is close to the solubility limit in Zr matrix.
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“To know is to know that you know nothing. That is the meaning of true knowledge”

Confucius