Fabrication of Zirconium Alloy Cladding Tubes and Other Fuel Assembly Components for Water-Cooled Reactors

Workshop on Modeling and Quality Control for Advanced and Innovative Fuel Technologies

Lecture given at International Centre of Theoretical Physics in Trieste on November 22, 2005

Hans G. Weidinger, Nürnberg/Germany
Zr-Materials
  Zr Basics
  Zr-Materials for LWRs

Fabrication:
  Conversion of Zr-Sand to Zr-Chloride/-Fluoride
  Hf/Zr Separation
  Reduction of ZrCl₄/ ZrF₄
  Alloying– Melting
  Hot Deformation
  Beta Quenching
  Cold Deformation
BASICS OF ZIRCONIUM

Basic physical/chemical properties,

Crystallographic Structure and Texture

Chemical Composition of Zr and Standard Zr-Alloys

Phases, Precipitates

Basic Characteristics of Improved and Advanced Zr-Alloys
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>40</td>
</tr>
<tr>
<td>Atomic Weight</td>
<td>91.22</td>
</tr>
<tr>
<td>Density</td>
<td>6.5 g/cm²</td>
</tr>
<tr>
<td>Elasticity Module</td>
<td>96,000 MPa</td>
</tr>
<tr>
<td>Melting Point</td>
<td>1875°C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>3577°C</td>
</tr>
<tr>
<td>Allotropic Modification</td>
<td>865°C</td>
</tr>
<tr>
<td>Linear Thermical Expansion Coefficient</td>
<td>5.8x10⁻⁶/°C</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>0.067 cal /g/°C</td>
</tr>
<tr>
<td>Specific Electrical Resistance</td>
<td>40 μΩ/cm</td>
</tr>
<tr>
<td>Macroscopic Cross-Section for Thermical Neutrons</td>
<td>0.0079 cm⁻¹</td>
</tr>
</tbody>
</table>

HEXAGONAL ZR-CRYSTAL

C-AXIS

Pyramid Gliding Layer (1011)

A-AXIS

Prism Gliding Layer (1010)

Twin Layer (1022)

C-AXIS

Twin Layer (1012)
CRYSTAL TEXTURE IN ZR ALLOY CLADDING TUBES

Unit cell hexagonal close-packed structure of Zircaloy

Circumferential Texture of basal poles
Random Texture of basal poles
Radial Texture of basal poles
Usual Texture of basal poles in cladding tube

### Commercial Zr-Materials for LWRs

<table>
<thead>
<tr>
<th>Material</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircaloy-2</td>
<td>BWR FR cladding, with internal liner (ZrFe, ZrSn, „Triclad“)</td>
</tr>
<tr>
<td>Zircaloy-4</td>
<td>BWR fuel structure (spacers, channels)</td>
</tr>
<tr>
<td></td>
<td>PWR FR cladding &amp; FA structure (classic)</td>
</tr>
<tr>
<td>M5</td>
<td>PWR FR cladding &amp; FA structure (advanced)</td>
</tr>
<tr>
<td>ELS-Duplex</td>
<td>PWR FR cladding</td>
</tr>
<tr>
<td>ZIRLO™</td>
<td>PWR FR cladding &amp; FA structure (advanced)</td>
</tr>
<tr>
<td>E110</td>
<td>WWER FR cladding</td>
</tr>
<tr>
<td></td>
<td>WWER structure</td>
</tr>
</tbody>
</table>
## Zircaloy Composition

<table>
<thead>
<tr>
<th>Alloy-Element</th>
<th>Zircaloy-2</th>
<th>Zircaloy-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin</td>
<td>1.20 - 1.70</td>
<td>1.20 - 1.70</td>
</tr>
<tr>
<td>Iron</td>
<td>0.07 - 0.20</td>
<td>0.18 - 0.24</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.05 - 0.15</td>
<td>0.07 - 0.13</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.03 - 0.08</td>
<td>-</td>
</tr>
<tr>
<td>Fe+Cr+Ni</td>
<td>0.18 - 0.38</td>
<td>-</td>
</tr>
<tr>
<td>Fe+Cr</td>
<td></td>
<td>0.28 - 0.37</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.09 - 0.16</td>
<td>0.09 - 0.1</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.005-0.012</td>
<td>0.005-0.012</td>
</tr>
</tbody>
</table>
**ADVANCED ZR ALLOYS FOR PWR COMMERCIALY INTRODUCED**

<table>
<thead>
<tr>
<th>Company</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRAMATOME</td>
<td>„M5“: Zr 1 Nb solid tube, with optimized chemical composition and „low temperature“ fabrication process, recrystallized</td>
</tr>
<tr>
<td>SIEMENS</td>
<td>„ELS 0.8 Duplex“: OD-Liner with Zry-4 with 0.8 Sn on standard Zircaloy-4, fabrication similar to optimized Zircaloy-4</td>
</tr>
<tr>
<td>WESTINGHOUSE</td>
<td>„ZIRLO™“: Zr1Nb1Sn 0.1Fe solid tube, with special heat treatments</td>
</tr>
<tr>
<td>Element</td>
<td>Tolerable</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td>wt%</td>
</tr>
<tr>
<td>Niobium</td>
<td>0.9 - 1.1</td>
</tr>
<tr>
<td>Tin</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Iron</td>
<td>0.05</td>
</tr>
<tr>
<td>Oxygen</td>
<td>≤ 0.1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>≤ 0.006</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>≤ 0.0015</td>
</tr>
<tr>
<td>Carbon</td>
<td>≤ 0.02</td>
</tr>
<tr>
<td>Silicon</td>
<td>≤ 0.02</td>
</tr>
<tr>
<td>Hafnium</td>
<td>≤ 0.05 (0.01)</td>
</tr>
</tbody>
</table>
PHASES, CRYSTALLOGRAPHIC STRUCTURE, DEFORMATION MECHANISMS OF ZIRCALOY

PHASE DIAGRAM OF THE SYSTEM Zr - Nb
IN TEMPERATURE RANGE 600 - 900°C,
SECTION Nb: 0 - 14%

ACC. BETHUNE AND WILLIAMS
# ADVANCED CLADDING TUBES FOR BWR
COMMERCIALY INTRODUCED

<table>
<thead>
<tr>
<th>Company</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ABB</strong></td>
<td>Sn Barrier: Zircaloy-2 solid tube (heat treatments „LK-2 or LK-3) plus</td>
</tr>
<tr>
<td></td>
<td>Sn-alloyed liner on ID (0,25% Sn)</td>
</tr>
<tr>
<td><strong>GENERAL ELECTRIC</strong></td>
<td>„Classical Barrier“: Zircaloy-2 solid tube plus</td>
</tr>
<tr>
<td></td>
<td>Zr-(unalloyed) liner on ID (400 ppm Fe, &lt; 600 ppm O)</td>
</tr>
<tr>
<td><strong>TRICLAD™</strong></td>
<td>Zircaloy-2 solid tube plus</td>
</tr>
<tr>
<td></td>
<td>Zr-(unalloyed) liner on ID (400 ppm Fe, &lt; 600 ppm O) plus</td>
</tr>
<tr>
<td></td>
<td>2nd Zircaloy-2 liner; base tube with ex (α+β)-quenching on OD-layer</td>
</tr>
<tr>
<td><strong>SIEMENS</strong></td>
<td>Fe-Barrier: Zircaloy-2 solid tube plus</td>
</tr>
<tr>
<td></td>
<td>Fe-alloyed liner on ID (0,4% Fe)</td>
</tr>
</tbody>
</table>
### ADVANCED ZR ALLOYS FOR PWR AND WWER COMMERCIAL PROPOSED

<table>
<thead>
<tr>
<th>FRAMATOME</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>„M4“:</td>
<td>Zr 0.5 Sn 0.6 Fe 0.4 V solid tube, fabrication similar to optimized Zry-4, fully recrystallized</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SIEMENS</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr1Nb</td>
<td>OD-Liner solid tube, partially recrystallized, with special heat treatment</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>WWER (RBMK)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>E-635</td>
<td>Zr1.2Nb1Sn 0.4 Fe solid tube with special heat treatments</td>
<td></td>
</tr>
</tbody>
</table>
FABRICATION

Basic Differences West - East
Conversion of Zr-Sand to Zr-Chloride/-Fluoride
Hf/Zr Separation
Reduction of ZrCl₄/ ZrF₄
Alloying– Melting
Hot Deformation
Beta Quenching
Cold Deformation
Zirkon Sources

Zr material fabrication everywhere in the world starts from the mineral “Zirkon” which occurs very frequently all over the world as ZrSiO$_2$.

Western production normally uses beach sand from Australia and South Africa. For example Framatome-ANP in France buys approximately 50% of its demand each from both countries. And it receives it already ground to a fine powder (“flour”).

Zirkon from Russia the Ukraine is used for Eastern production.
Basic Fabrication Differences West – East

Western Technology
There are 3 companies producing nuclear grade Zr-products:
   Wah Chang and Western Zirconium in the US, and
   Framatome-ANP in France
In all three companies the fabrication from the raw material Zr-sand to the alloyed metallic ingot is based on a Zr-tetrachloride technology.
There is only one difference between production in the US and France:
   the Zr/Hf separation technology.

Eastern Technology
There are 2 companies producing nuclear grade Zr-products:
   Chepetsky Mechanical Plant in Russia, and
   SSPE-Tsircony Plant in Ukraine
The Russian fabrication from Zr-raw material to the alloyed metallic ingot is based on a Zr-tetrachloride technology.
The Ukrainian fabrication from Zr-raw material to the alloyed metallic ingot is based on a Zr-tetrafluoride technology.
# Technological Differences between Western and Russian Production

<table>
<thead>
<tr>
<th>Fabrication Steps</th>
<th>Western</th>
<th>Russian</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting Material</td>
<td>Beach Sand from Australia</td>
<td>Ore from open pit in Ukraine</td>
</tr>
<tr>
<td>Hf Separation</td>
<td>Extractive Distillation</td>
<td>Fractional Crystallization</td>
</tr>
<tr>
<td></td>
<td>Liquid-Liquid Extraction</td>
<td></td>
</tr>
<tr>
<td>Reduction to Metal</td>
<td>Kroll Process: Reduction by Mg</td>
<td>Molten Salt Electrolysis</td>
</tr>
<tr>
<td>Refinement</td>
<td>None</td>
<td>Zr-Iodide Process</td>
</tr>
<tr>
<td>Zirconium</td>
<td>≤ 30% Scrap + Zr Sponge</td>
<td>10% Scrap + 30% Crystal Bar + 60 % Zr-Powder</td>
</tr>
</tbody>
</table>

The processes following, from melting to final product are similar, with differences in details.
Fabrication Sequences to Produce Zr-Alloy Material in Glasov, Russia

1. Van Arkel Process
2. Jodide-Zr
3. 10% Scrap
4. 30%
5. 60%
6. + Nb Powder (& Other Alloy Elements)
7. Electrode Preparation
8. 1st & 2nd Melting
9. Zr-Alloy Ingot
10. Scrap
11. ZrSiO₄ + K₂SiF₆
12. Fractional Recrystallization
13. Zr - Hf Separation
14. Reduction
15. + KCl Electrolysis, ~ 800°C
16. Leaching, Granulating, Grinding Carbonate- & Acid-Treatment
17. Blending, Mixing, Pressing to Briquets, Sintering
18. Vacuum Arc Melting
19. Machining, Surface EB-Melting
20. Further Processing

Source: Chepetsky Mechanical Plant, Glasov, Russia
Fabrication Sequences to Produce Zr-Alloy Material in the Ukraine

1. Thermochemical Conversion of Zr-Ore
   - Zr-Silicate
     (+ Na-Carbonate; Fusion)
   - Na-Zirconate
     (+ H₂O + HNO₃; Leaching)
   - Zr-Nitrate

2. Separation of Hafnium
   - Zr-Nitrate
     (+ HF₃; Precipitation)
   - Zr-Tetrafluoride (monohydrate)
     (+ Ca + Nb; Reduction and Alloying)
   - Zr-Raw Metal
     (Electron-Beam Melting)
   - Zr₁Nb Ingot

3. alloying, Reduction to Metal, Melting

Source: SSPE-Tsircony Plant, Dnjeprodzerzinsk, Ukraine
Western Fabrication Steps from Raw Material to Zr-Alloy Ingot

Conversion of Zr-Sand to Zr-Chloride
Hf/Zr Separation
Reduction of ZrCl$_4$
Alloying– Melting
Conversion of Zr Sand to Zr-Tetrachloride

Carbo-Chlorination

The first step after physical enrichment is a chemical conversion of the natural raw-material to Zr-tetrachloride which is performed by a carbo-chlorination (fig. 1) according to the reaction:

\[
ZrO_2 (+SiO_2 + HfO_2) + 2C + 2Cl_2 \rightarrow ZrCl_4 (+SiCl_4 + HfCl_4) + 2 CO
\]

With selective condensation the the mixed Zr- and Hf- chloride is separated from the Si-chloride, while the residual gases, particularly carbon monoxide are finally released to the atmosphere or recycled to another chemical plant.
Conversion of Zirkon-Sand to ZrCl₄ by Carbo-Chlorination

Source: Framatome-ANP
Carbo-chlorination of Zr-SAND and Hf-Separation
Western Technologies

Source: Framatome-ANP
Zirconium and Hafnium have to be separated for nuclear purposes. This is performed in the US at Wah Chang and Western Zirconium by liquid-liquid extraction.

For the **liquid-liquid extraction** process

The mixed ZrHf-chloride is dissolved in hydrochloric acid.

The Zr and Hf ions are complexed with ammonium-thio-cyanate to Zr(SNC)_2/Hf (SNC)_2.

Hf is extracted with methylisobutyl ketone (MIBK) in a counter current liquid-liquid extraction system.

The aqueous phase, containing the Zr, is mixed with sulfuric acid to precipitate the Zr as hydroxide with the addition of ammonium hydroxide.

After filtering the Zr-hydroxide is calcined to ZrO₂.

Hf is stripped off from the MIBK with hydrochloric acid and recovered to oxide similarly as Zr.

For this separation process the carbo-chlorination has to be repeated to produce a Hf-"free" ZrCl₄ to be reduced to Zr-metal (see Kroll process).

With this process Hf contents of 40 – 50 ppm remaining in the Zr could be achieved already years ago.
Hf Separation by Liquid-Liquid Extraction with MIBK

HSCN/MIBK

aqueous phase
ZrO(SCN)$_2$

HCl

ZrOCl$_2$, Hf < 50 ppm

organic phase
HfO(SCN)$_2$

H$_2$SO$_4$

HfO(SO$_4$)$_2$, Zr < 4.5%

2nd cycle

Zr/Hf oxy-cloride

NH$_3$SCN

ZrOCl$_2$/HfOCl$_2$

Zr/Hf thio-cyanate

ZrO(SCN)$_2$/Hf(SCN)Cl$_2$
Hf-Separation by Liquid-Liquid Extraction

Raw ZrCl₄ (with Hf)
Water

ZrOCl₂
HfOCl₂

Thiocyanate
SNC NH₄

HfO(SNC)₂

MIBK

ZrOCl₂

SO₂ H₂

NH OH

Zr(OH)₂
CALCINATION

ZrO₂ (Hf-free)

Source: CEZUS
Hf/Zr Separation
Extractive Distillation

Zirconium and Hafnium have to be separated for nuclear purposes. This is performed in France by extractive distillation.

With the **extractive distillation** process Hf is removed by dissolving the ZrHf-chloride in potassium-aluminum chloride (KCl-AlCl₃).

A solvent made of molten KCl-AlCl₃, is circulated from the top to the bottom (<10.000 l/h).

Vapor of ZrCl₄ (500°C) rises in a counterflow from bottom up.

The vapor going up is progressively enriched in HfCl₄.

The liquid going down progressively looses Hf-content.

The ZrCl₄ is stripped, cooled and condensed in a nitrogen stream (50m3/h).

The efficiency of the distillation process has been published as 98% as compared with the „liquid-liquid“ process with 89% efficiency.

Today < 40 ppm Hf in Zr are normal commercial quality from both types of processes.
Hf-SEPARATION
BY EXTRACTIVE DISTILLATION

## ZrCl₄ Nuclear-Grade Composition Referred to Zirconium Basis

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>Liquid/Liquid Dehafniation (ppm)</th>
<th>Dehafniation Extrac Distillation (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>&lt; 120</td>
<td>&lt; 120</td>
</tr>
<tr>
<td>P</td>
<td>&lt; 100</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Hf</td>
<td>30/80</td>
<td>35/60</td>
</tr>
<tr>
<td>Al</td>
<td>5/50</td>
<td>10/60</td>
</tr>
<tr>
<td>Na</td>
<td>&lt; 50</td>
<td>&lt; 50</td>
</tr>
<tr>
<td>Si</td>
<td>&lt; 30</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Ca, Fe, Ti</td>
<td>&lt; 20</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>Cr, Cu, Mg, Mn, Mo, Ni, Pb, Sn, V</td>
<td>&lt; 10</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>U</td>
<td>&lt; 3</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>B</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

New Process for Zirconium and Hafnium Separation

Moulin et al., Zirconium in the Nuclear Industry, 6th Int'l Symp., ASTM STP 824, 1984,
Reduction of ZrCl₄

Regardless which Zr/Hf separation process is used the next step in commercially producing Zr-alloys in the West is the reduction of ZrCl₄ to metallic Zr.

The basic chemical process is

\[ \text{ZrCl}_4 + 2 \text{Mg} \rightarrow 2\text{MgCl}_2 + \text{Zr} \]

This process is called in honor of its inventor the “Kroll process”.

The already rather pure Zr-tetrachloride is reduced to metallic Zr by using metallic Mg as reductant. The purity of the Mg is very important not to enter new impurities in the metallic Zr.

This process ends up with a very porous Zr-metal, therefore called Zr “sponge”.

Large pieces of Zr sponge are crushed mechanically into smaller sizes.

Besides some few volatile elements like chlorine and magnesium, all of the impurities present at this stage will remain with the Zr and therefore also end up in the Zr-alloy. The most common impurities are iron, nitrogen, oxygen, and aluminum.
Kroll - Process:
Reduction of ZrCl₄ by Magnesium

Source: Framtome-ANP
Alloying – Electrode Preparation – Melting

Due to the reactivity of the metal and its high melting temperature (1,850 °C) an economic production uses the vacuum arc process with a consumable electrode for melting. This melting process is performed twice or three times depending on the experience of the producer and on customer requirements.

The necessary first step the electrode preparation for the first melting process.

The electrode contains three different sources of material: Zr-sponge, alloying elements, recycled material.

The recycled material today originates from in house production only. Nevertheless the recycling process consists of a sophisticated sequence of purification and control steps.

Today the ratio is much more reduced (about 25 – 30 % or less).

The details of the electrode preparation vary between the various producers.

At Framatome-ANP the electrode is built with briquettes weighing 50 to 60 kg, each briquette containing all the constituents of the load in the required proportions. These briquettes are compressed to compacts with a hydraulic press.

The compacts then are assembled by electron beam welding to an approximately 3 ton electrode. Under these conditions generally triple melting is applied to obtain final ingots with about 6 tons size.
Electrode Preparation

Zircaloy Electrode after Electron-Beam Welding

Source: Framatome-ANP
Melting

Melting is performed in a vacuum arc furnace with consumable electrode and a water cooled copper crucible.

Melting temperature is 1850°C.

A rotating magnetic field is applied to the molten zone for improved mixing.

Depending on the customer 2 or 3 melting steps are applied.

1st and 2nd melting occurs under vacuum $10^{-2}$ to $10^{-3}$ Torr, 3rd melting occurs under vacuum $10^{-4}$ Torr.

Melting requires a lot of practical experience to minimize the radial and longitudinal variation of alloying elements, since the solubility of the various elements is different in the liquid and in the solid phase.
Melting of Zr-Alloys by the Consumable Electrode Process

[Zirconium Alloy Fuel Clad Tube - Sandvik Special Metals Corp. (1989) p. 27]
Melting of Zr-Alloys by the Consumable Electrode Process

6t Ingots of Zry-4, as Melted

Source: Framatome-ANP
Western Fabrication Steps from Zr-Alloy Ingot to Final Products

- Hot Deformation
- Forging
- Extrusion
- Beta-Quenching
- Cold Deformation
Hot Deformation – Beta Quenching –

The as cast final ingot has a fusion structure to be deformed and also has to be reduced to smaller dimensions stepwise.

For this purpose several hot deformations are necessary.

In the West replaced by modern high efficiency hot pre-forging.

These processes reduce the original outer diameter of the final ingot of ~ 630 mm to finally ~180 mm.

Beta quenching is an essential step for all Zircaloy material production.

It may be performed before the $\alpha$–forging or before the hot extrusion.

For tubular material a hot extrusion process is added:

after machining the hot deformed logs into billets with a hole drilled in.

With this process tube hollows are fabricated which are the starting product for the cold deformation processes ending up as cladding or guide tubes for nuclear fuel.
Hot Deformation
Forging

The finally melted ingot is converted into billets for extrusion by hot forging.

Two processes have to be distinguished:

- Forging after heating into the $\beta$-phase temperature range (\(~1050°C\)),

  This process is used for the first steps of heavy reduction of dimensions down to octagons of \(~350\) mm.

- Forging after heating into the $\alpha$-phase temperature range (\(<750°C\))

  This process is used for the smaller dimensions. There are two purposes for working in the $\alpha$-phase temperature range:
  
  - breaking the fusion structure to achieve high structural homogeneity, and
  - achieving a given value for the $\Sigma A$ parameter (= “cummulative annealing parameter”) already in that stage of fabrication, as required by the customer. This $\Sigma A$ parameter plays an important role to control the in-pile corrosion of Zircaloy (-2 and-4). In this case the $\beta$-quenching is performed before these forging steps.
Hot Deformation
Extrusion

After final forging to ~180 mm diameter the log is being cut and machined to the size where from the extrusion process starts to form a tube hollow which is the starting work-piece for the (cladding or guide tube) fabrication by cold deformation.

The machining comprises the adjustment of the outer diameter by turning and the drilling of a hole into the billet.

The extrusion process is performed in the $\alpha$-phase temperature range.

There are very strict geometrical requirements like straightness and wall thickness, in particular with regard to concentricity,

For cladding tube fabrication today typically outer diameter between 80 to 85 mm are used and a high wall thickness, e.g. a dimension like 80 x 14 mm (O.D. x Wall).
High Load/ High Speed Press Forging

Photos: H.G. Weidinger, by courtesy of Framatome-ANP
Beta-Quenching is one of the most important process steps from alloying/melting to the finish of the final product.

On one hand, this process step facilitates to make the material "forget" the influence of all previous processing. On the other hand, it sets the starting conditions for all subsequent thermal-mechanical processes which are now all kept within the temperature range of the alpha-phase.

Beta-quenching consists of the following four equally important process phases:

1. Heating up by inductive heating or by radiation heating in an (electrically heated) furnace –
2. Temperature Holding (Soaking) in the beta-phase temperature range (< 1050 °C)
3. Transfer from the heating device (electrical furnace, induction heating, etc) to the quenching facility (water bath)
4. Quenching, i.e. the material is cooled rapidly from the beta-phase temperature range to alpha-phase temperature range (room temperature)
KEY PROCESSES
„BETA -QUENCHING“

H. G. Weidinger
Cold Deformation I

From Tube Hollow to Final Tubes:

FR cladding tubes,
Structural tubes, like guide tubes (PWR fuel) or water rods (BWR fuel)

For fabricating cladding tubes

today starting dimensions of 80 to 85 mm O.D are used and
the cold deformation (i.e. rocking = pilgering) occurs in four steps
from tube hollow to final cladding tube.

Important parameters for these cold deformation steps are
the degree of cold work and
the “q-factor”: \( \Delta \text{ wall-thickness} : \Delta \text{ O.D.} \)

After each cold deformation step
an intermediate annealing is necessary to recrystallize the material
that became very hard and brittle during the cold deformation.

Normally an annealing procedure at \( \sim 750^\circ \text{C}/2\text{h} \) is used.

Final fabrication steps are:
final annealing
finishing
Cold Deformation
Pilgering

During the cold pilger-rolling process, the tube is reduced both in diameter and in wall thickness by means of two contiguous grooved rolls mounted one on top of the other which pass it over a conical mandrel.

Source Frameome-ANP/NRG
Optimizing the Texture by Modified Pilgering Sequence


Cold Deformation Steps to Fabricate Cladding Tubes

Old standard fabrication PWR cladding tube

- Texture
- Grain size

Texture optimized fabrication PWR cladding tube

- Texture
- Grain size

ASTM Nor. 13
4,0 µm

Q = 1,68
Q = 1,03
Q = 2,81
Q = 1,02
Q = 1,65
Q = 1,34
Q = 5,9
Q = 1,03
Q = 1,02
Q = 1,65
Q = 1,34
Q = 5,9
Q = 1,03
Q = 1,02
Q = 1,65
Q = 1,34
Q = 5,9
Q = 1,03
Q = 1,02
Q = 1,65
Q = 1,34
Q = 5,9
E = 76,1%
E = 81,0%
E = 76,1%
E = 81,9%
E = 74,6%
E = 69,7%
E = 71,3%
E = 69,7%
E = 74,6%
E = 81,9%
„Alpha-Annealing“ in Vacuum

Technological Background for Adequate Vacuum Annealing

Schematic Depiction of The Local Difference in Temperature vs. Time History During Vacuum Annealing of Zircaloy Tubes

H.G. Weidinger
Cold Deformation
Zr Sheet Products

Application
Spacer grid prematerial (BWR & BWR fuel structure),
BWR fuel channel sheets

For fabricating sheets
hot deformation (rolling or forging) to starting dimension for
cold deformation (rolling with or without axial stress)) occurs in many steps

Important parameters for these cold deformation steps are
the degree of cold work and
the rolling direction

After each cold deformation step
an intermediate annealing is necessary to recrystallize the material
that became very hard and brittle during the cold deformation.

Normally an annealing procedure at ~750°C/2h is used.

Final fabrication steps are:
final annealing
finishing
Zr-Sheet Production

Basic Process Flow Outline for Sheet Fabrication from Beta - Quenching

- Beta-quenching of plate
- hot rolling in alpha-region
- cold rolling in several steps
- intermediate alpha-annealing
- final alpha-annealing
- finishing (surface)
Cold Rolling

Cold Rolling with Axial Stress

Source: Wah Chang