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

CONTENT

BASICS OF ZIRCONIUM

Basic physical/chemical properties,

Crystallographic Structure and Texture

Chemical Composition of Zr and Standard Zr-Alloys

Phases, Precipitates

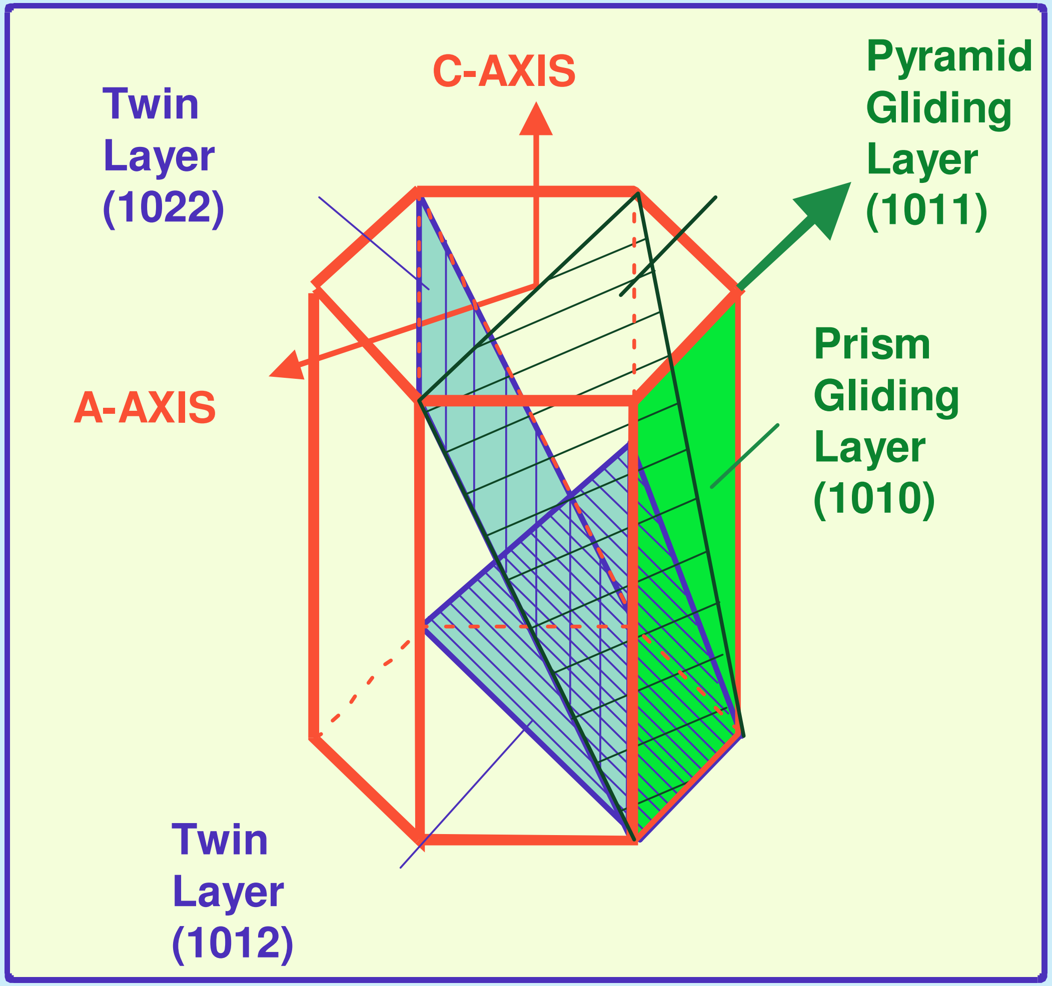
Basic Characteristics of Improved and Advanced Zr-Alloys

PHYSICAL PROPERTIES

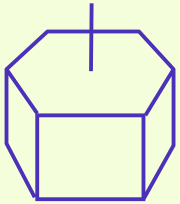
Atomic Number	40
Atomic Weight	91,22
Density	6,5 g/cm^2
Elasticity Module	96.000 MPa
Melting Point	1875°C
Boiling Point	3577°C
Allotropic Modification	865°C
Linear Thermical Expansion Coefficient	$5,8x10^{-6}$/°C
Specific Heat	0,067 cal /g/°C
Specific Electrical Resistance	40 μΩ/cm
Macroscopic Cross-Section for Thermical Neutrons	0,0079 cm^{-1}

Acc. J.H. Schemel "ASTM Manual on Zirconium and Hafnium", ASTM STP 639 (1977) p.4

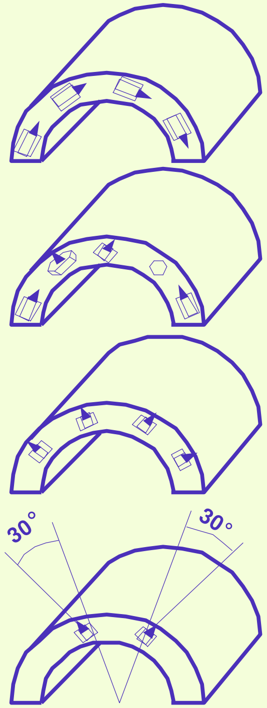
HEXAGONAL ZR-CRYSTAL



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

By SSM "Zirconium Alloy Fuel Clad Tubing-Engineering Guide“ 5th Edition Press Craft, Pasco/WA,USA(1989)

Commercial Zr-Materials for LWRs

Material	Application
Zircaloy-2	BWR FR cladding, with internal liner (ZrFe, ZrSn, „Triclad“)
Zircaloy-4	BWR fuel structure (spacers, channels) PWR FR cladding & FA structure (classic)
M5	PWR FR cladding & FA structure (advanced)
ELS-Duplex	PWR FR cladding
ZIRLO™	PWR FR cladding & FA structure (advanced)
E110	WWER FR cladding
	WWER structure

Zircaloy Composition

Alloy-Element	Zircaloy-2	Zircaloy-4
Tin	1.20 - 1.70	1.20 - 1.70
Iron	0.07 - 0.20	0.18 - 0.24
Chromium	0.05 - 0.15	0.07 - 0.13
Nickel	0.03 - 0.08	-
Fe+Cr+Ni	0.18 - 0.38	-
Fe+Cr		0.28 - 0.37
Oxygen	0.09 - 0.16	0.09 - 0.1
Silicon	0.005-0.012	0.005-0.012

ADVANCED ZR ALLOYS FOR PWR COMMERCIALLY INTRODUCED

FRAMATOME

„M5“: Zr 1 Nb solid tube, with optimized chemical composition and „low temperature“ fabrication process, recrystallized

SIEMENS

„ELS 0.8 Duplex“: OD-Liner with Zry-4 with 0.8 Sn on standard Zircaloy-4, fabrication similar to optimized Zircaloy-4

WESTINGHOUSE

„ZIRLO^{TM}“: Zr1Nb1Sn 0.1Fe solid tube, with special heat treatments

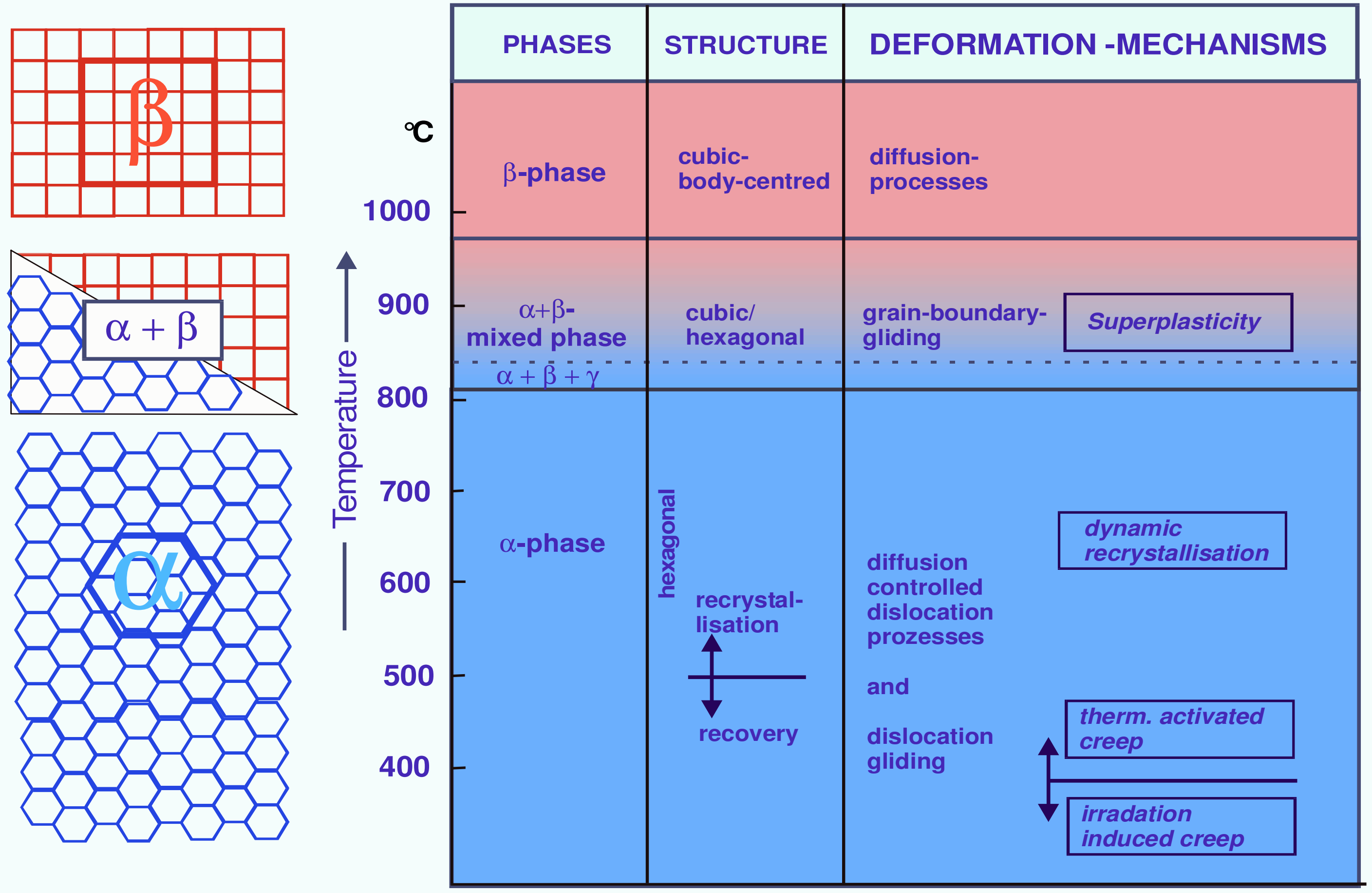
E 110 (Zr1Nb)
Chemical Composition Zr1Nb

Element	Tolerable wt%	Typical wt%
Niobium	0.9 - 1.1	0.95 - 1.10
Tin	≤ 0.05	< 0.001
Iron	≤ 0.05	0.014
Oxygen	≤ 0.1	0.05 - 0.07
Nitrogen	≤ 0.006	0.003 - 0.004
Hydrogen	≤ 0.0015	0-0004 - 0.0007
Carbon	≤ 0.02	0.003 - 0.007
Silicon	≤ 0.02	0.004 - 0.009
Hafnium	≤ 0.05 (0.01)	0.03 - 0.04 (< 0.008)

E-110 Alloy Cladding Tube Properties and Their Interrelation
With Alloy Structure – Phase Condition And Impurity Content

P.V. Shebaldov et.al., 12th ASTM Zr Conference,
Toronto, Canada, June 15 – 18, 1998

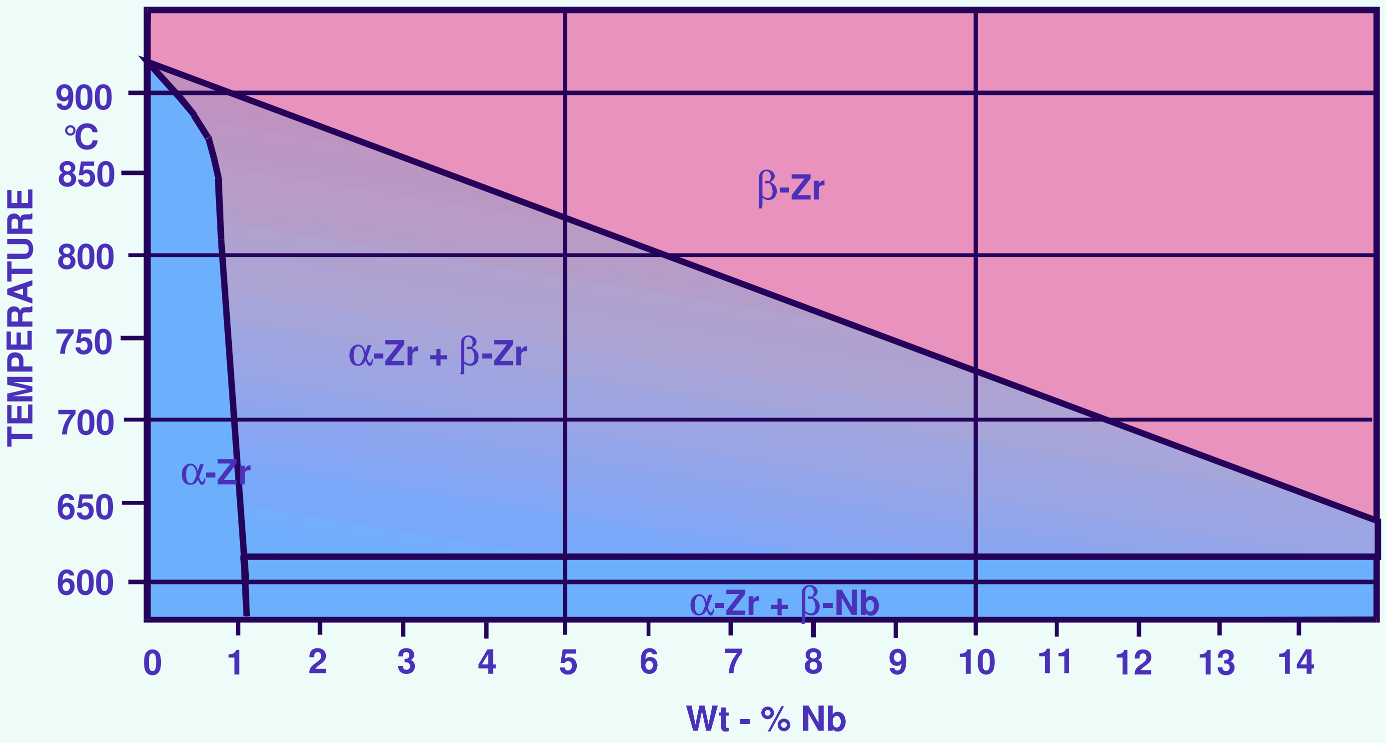
PHASES, CRYSTALLOGRAPHIC STRUCTURE, DEFORMATION MECHANISMS OF ZIRCALOY



PHASES	STRUCTURE	DEFORMATION -MECHANISMS	
β-phase	cubic-body-centred	diffusion-processes	
α+β-mixed phase	cubic/hexagonal	grain-boundary-gliding	*Superplasticity*
α-phase	hexagonal recrystallisation ↑ recovery ↓	diffusion controlled dislocation prozesses and dislocation gliding	*dynamic recrystallisation* *therm. activated creep* ↑ *irradiation induced creep* ↓

H.G. Weidinger et al., in Ilschner: „Density and Deformation under High Temerature", DGM, Oberursel, Germany (1983) pp. 137 ff.

PHASEDIAGRAM OF THE SYSTEM Zr - Nb
IN TEMPERATURE RANGE 600 - 900℃,
SECTION Nb: 0 - 14%



ACC. BETHUNE AND WILLIAMS

ADVANCED CLADDING TUBES FOR BWR COMMERCIALLY INTRODUCED

ABB

Sn Barrier	Zircaloy-2 solid tube (heat treatments „LK-2 or LK-3) plus Sn-alloyed liner on ID (0,25% Sn)

GENERAL ELECTRIC

„Classical Barrier“	Zircaloy-2 solid tube plus Zr-(unalloyed) liner on ID (400 ppm Fe, < 600 ppm O)
TRICLAD™	Zircaloy-2 solid tube plus Zr-(unalloyed) liner on ID (400 ppm Fe, < 600 ppm O) plus 2nd Zircaloy-2 liner; base tube with ex $(\alpha+\beta)$-quenching on OD-layer

SIEMENS

Fe-Barrier	Zircaloy-2 solid tube plus Fe-alloyed liner on ID (0,4% Fe)

ADVANCED ZR ALLOYS FOR PWR AND WWER COMMERCIALLY PROPOSED

FRAMATOME

„M4“:	Zr 0.5 Sn 0.6 Fe 0.4 V solid tube, fabrication similar to optimized Zry-4, fully recrystallized

SIEMENS

Zr1Nb	OD-Liner solid tube, partially recrystallized, with special heat treatment

WWER (RBMK)

E-635	Zr1.2Nb1Sn 0.4 Fe solid tube with special heat treatments

FABRICATION

Basic Differences West - East

Conversion of Zr-Sand to Zr-Chloride/-Fluoride

Hf/Zr Separation

Reduction of $ZrCl_4$/ ZrF_4

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.

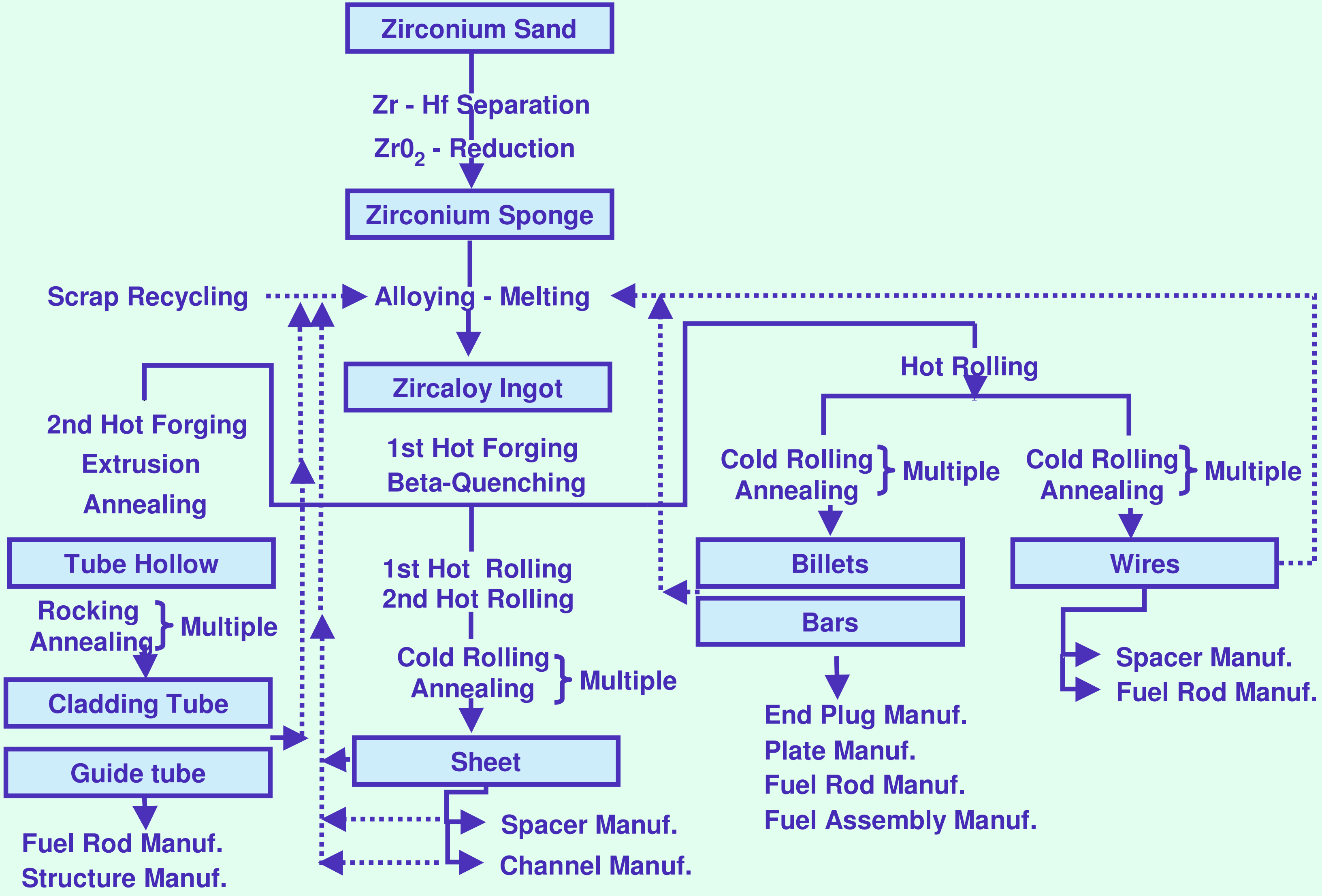
The Ukrainean fabrication from Zr-raw material to the alloyed metallic ingot is based on a Zr-tetrafluoride technology.

Technological Differences between Western and Russian Production

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

The processes following, from melting to final product are similar, with differences in details

MANUFACTURING ROUTES - WESTERN TECHNOLOGY OVERVIEW



Zirconium Sand

Zr - Hf Separation

ZrO_2 - Reduction

Zirconium Sponge

Scrap Recycling

Alloying - Melting

Zircaloy Ingot

1st Hot Forging

Beta-Quenching

2nd Hot Forging

Extrusion

Annealing

Tube Hollow

Rocking

Annealing } Multiple

Cladding Tube

Guide tube

Fuel Rod Manuf.

Structure Manuf.

1st Hot Rolling

2nd Hot Rolling

Cold Rolling

Annealing } Multiple

Sheet

Spacer Manuf.

Channel Manuf.

Hot Rolling

Cold Rolling

Annealing } Multiple

Billets

Bars

End Plug Manuf.

Plate Manuf.

Fuel Rod Manuf.

Fuel Assembly Manuf.

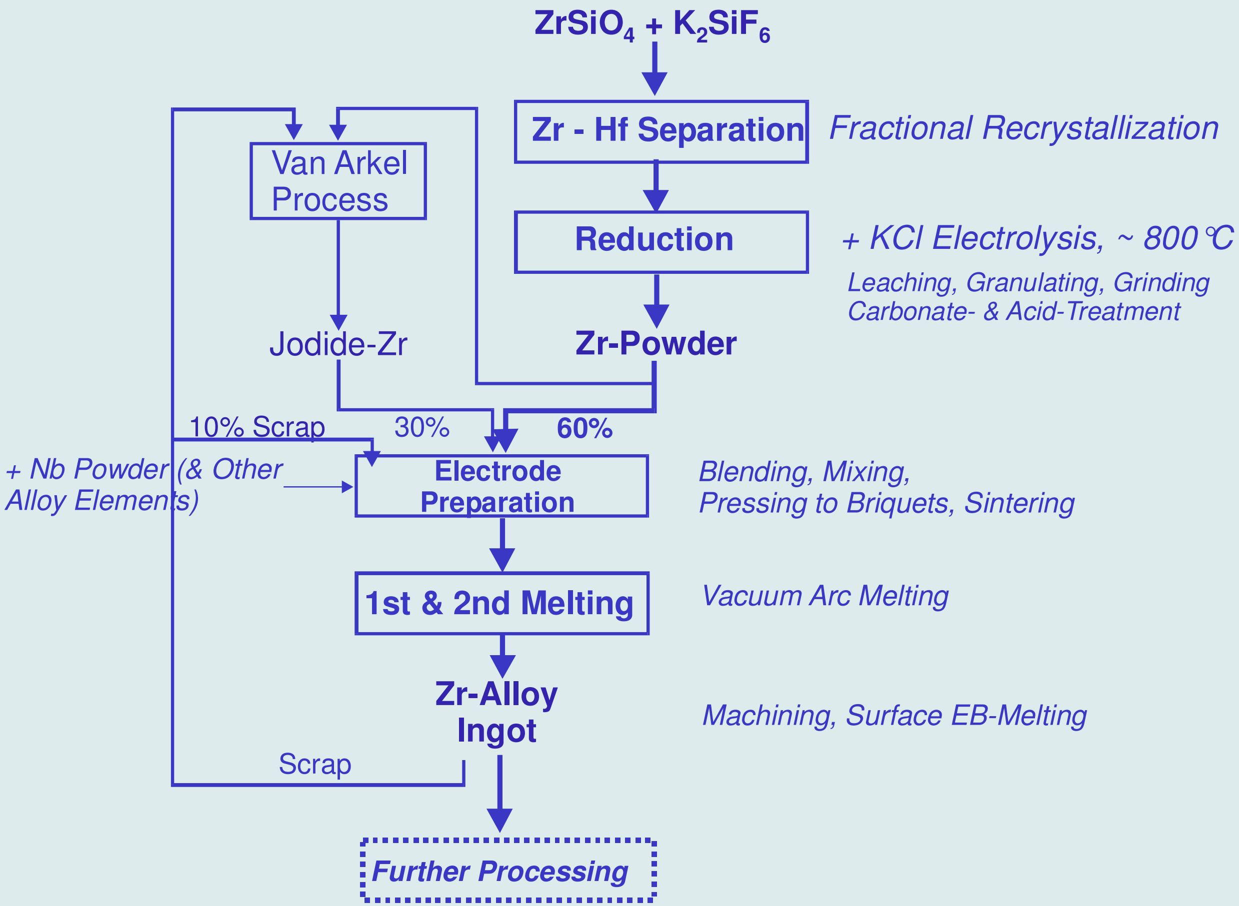
Cold Rolling

Annealing } Multiple

Wires

Spacer Manuf.

Fuel Rod Manuf.



$ZrSiO_4 + K_2SiF_6$

Zr - Hf Separation *Fractional Recrystallization*

Reduction *+ KCl Electrolysis, ~ 800 ℃*

Leaching, Granulating, Grinding
Carbonate- & Acid-Treatment

Zr-Powder

Van Arkel Process

Jodide-Zr

10% Scrap

30%

60%

+ Nb Powder (& Other Alloy Elements)

Electrode Preparation *Blending, Mixing, Pressing to Briquets, Sintering*

1st & 2nd Melting *Vacuum Arc Melting*

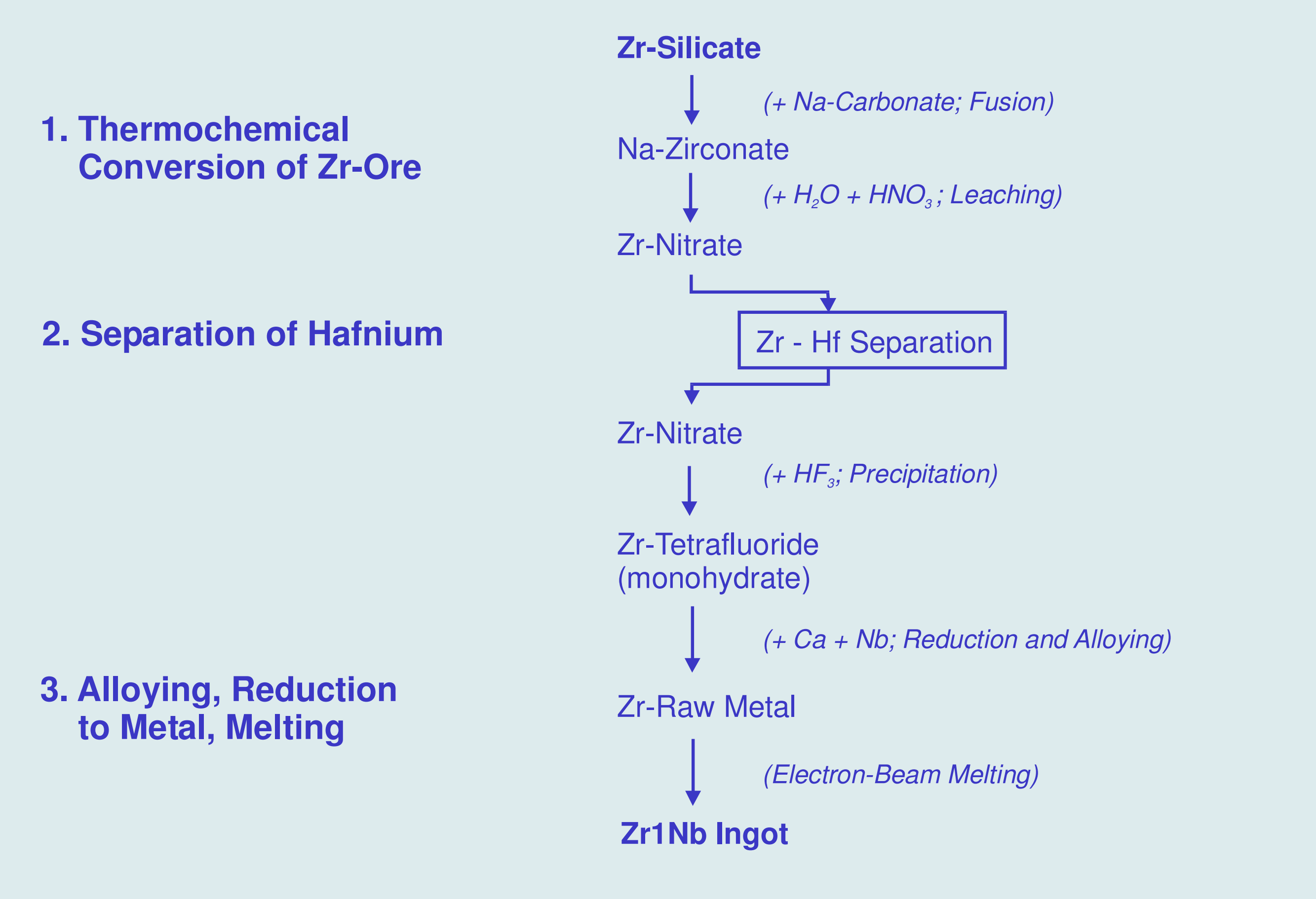
Zr-Alloy Ingot *Machining, Surface EB-Melting*

Scrap

Further Processing

Source: Chepetsky Mechanical Plant, Glasov, Russia

Fabrication Sequences to Produce Zr-Alloy Material in Glasov, Russia



1. Thermochemical Conversion of Zr-Ore

2. Separation of Hafnium

3. Alloying, Reduction to Metal, Melting

Zr-Silicate

(+ Na-Carbonate; Fusion)

Na-Zirconate

(+ H_2O + HNO_3; Leaching)

Zr-Nitrate

Zr - Hf Separation

Zr-Nitrate

(+ HF_3; Precipitation)

Zr-Tetrafluoride (monohydrate)

(+ Ca + Nb; Reduction and Alloying)

Zr-Raw Metal

(Electron-Beam Melting)

Zr1Nb Ingot

Fabrication Sequences to Produce Zr-Alloy Material in the Ukraine

Source: SSPE-Tsircony Plant, Dnjeprodzerzinsk, Ukraine

Western Fabrication Steps from Raw Matrial 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

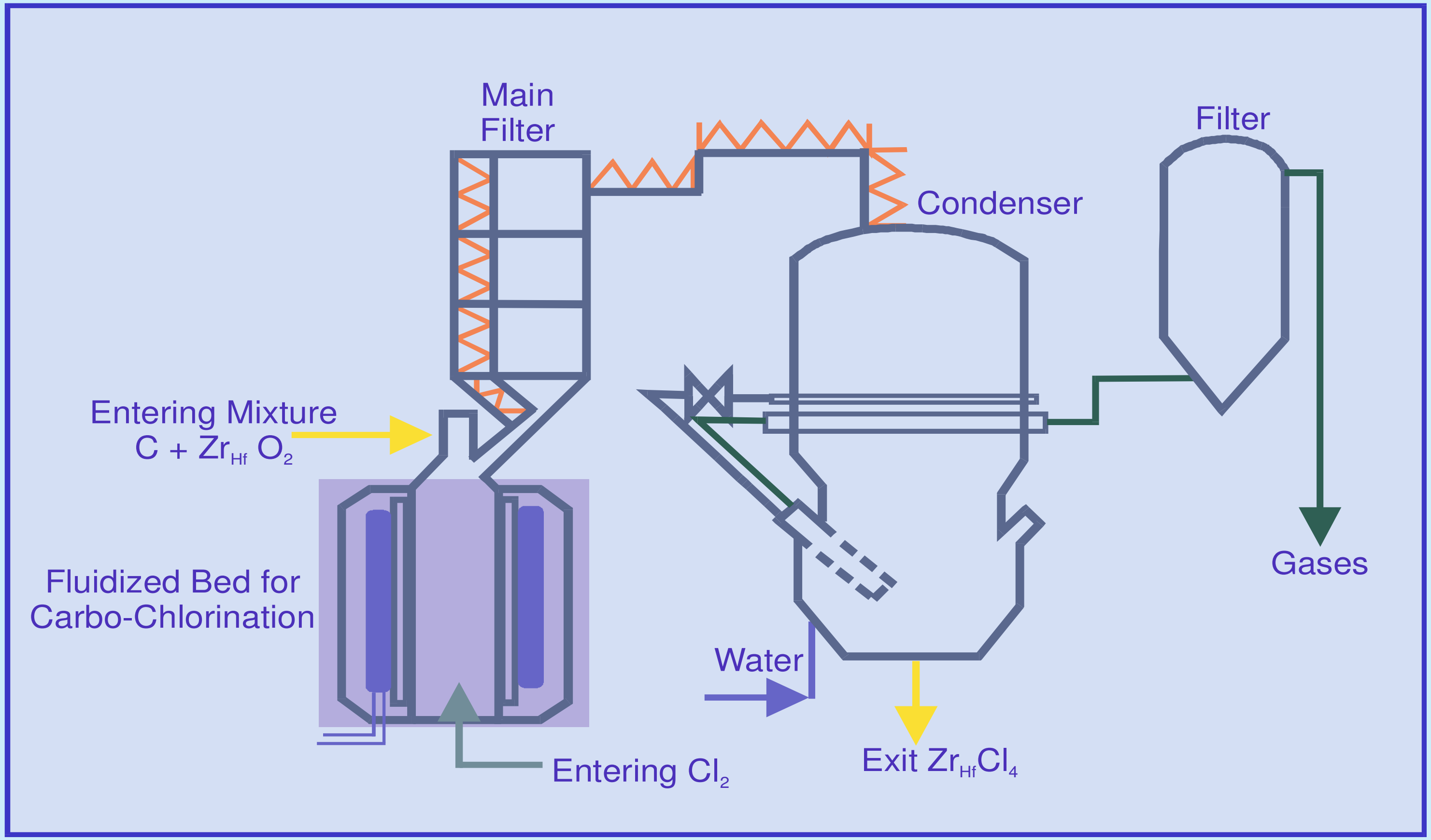
Carbo-Chlorination

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:

$$ZrO_2 \; (+SiO_2 + HfO_2) + 2C + 2Cl_2 \rightarrow ZrCl_4 \; (+SiCl_4 + HfCl_4) + 2\,CO$$

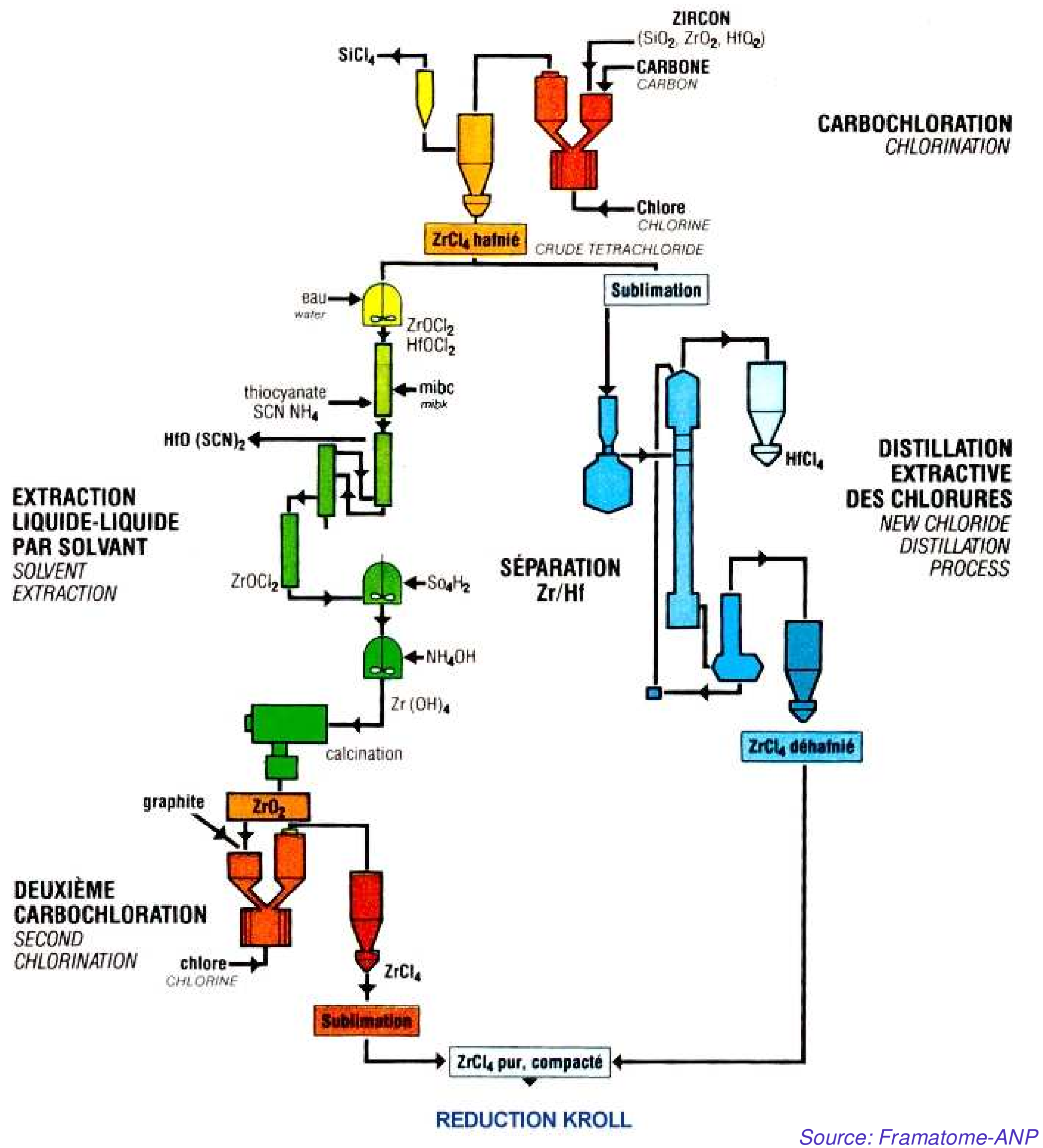
With selective condensation the the mixed Zr- and Hf- chloride is separated from the Si-chloride, while the residual gases, particularly carbon monoxide are finally released to the atmosphere or recycled to another chemical plant.

Conversion of Zirkon-Sand to $ZrCl_4$ by Carbo-Chlorination



Source: Framatome-ANP

Carbo-chlorination of Zr-SAND and Hf-Separation
Western Technologies



Source: Framatome-ANP

Hf/Zr Separation
Liquid-Liquid-Extraction

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.

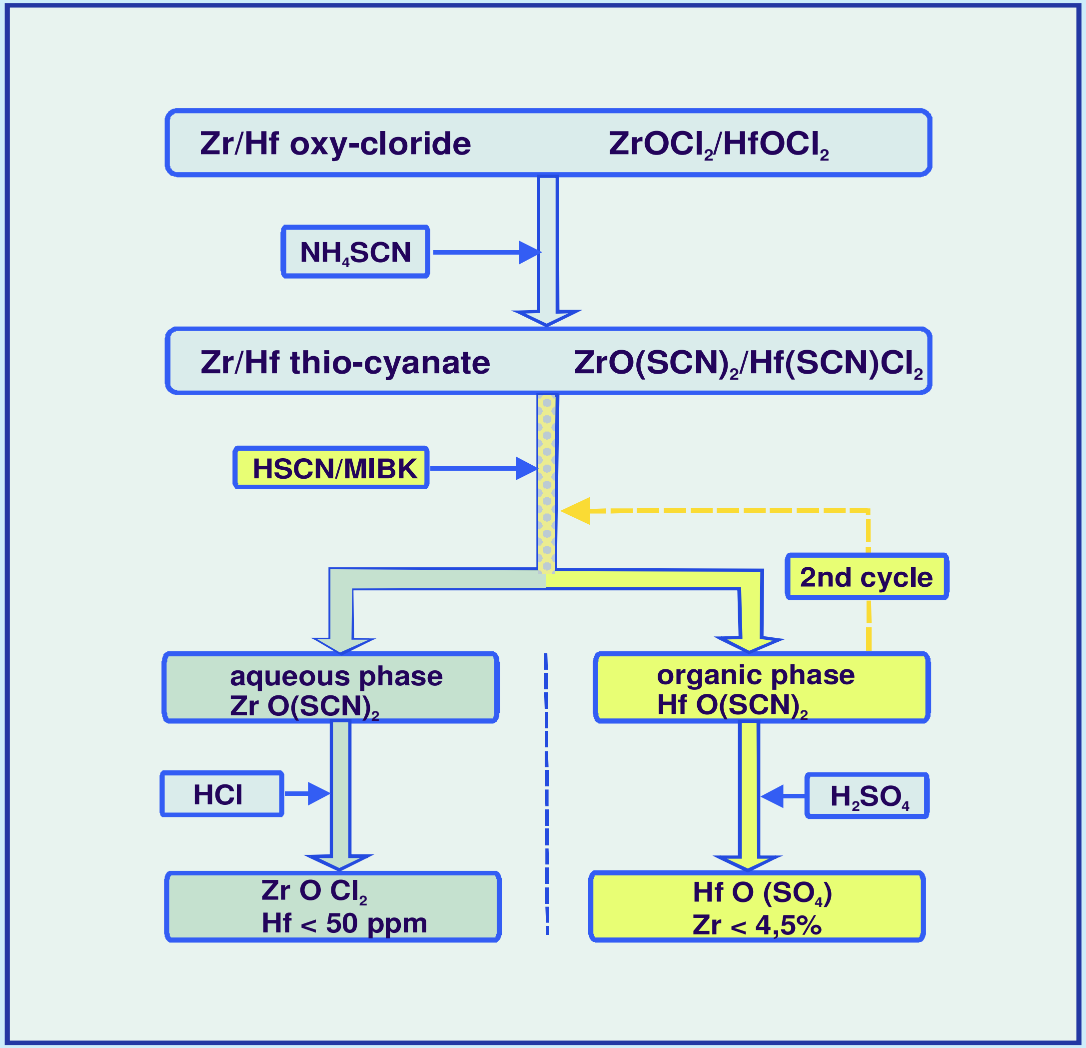
After filtering the Zr-hydroxide is calcined to ZrO_2.

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" $ZrCl_4$ 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



Zr/Hf oxy-cloride $ZrOCl_2/HfOCl_2$

NH_4SCN

Zr/Hf thio-cyanate $ZrO(SCN)_2/Hf(SCN)Cl_2$

HSCN/MIBK

2nd cycle

aqueous phase
$Zr\,O(SCN)_2$

organic phase
$Hf\,O(SCN)_2$

HCl

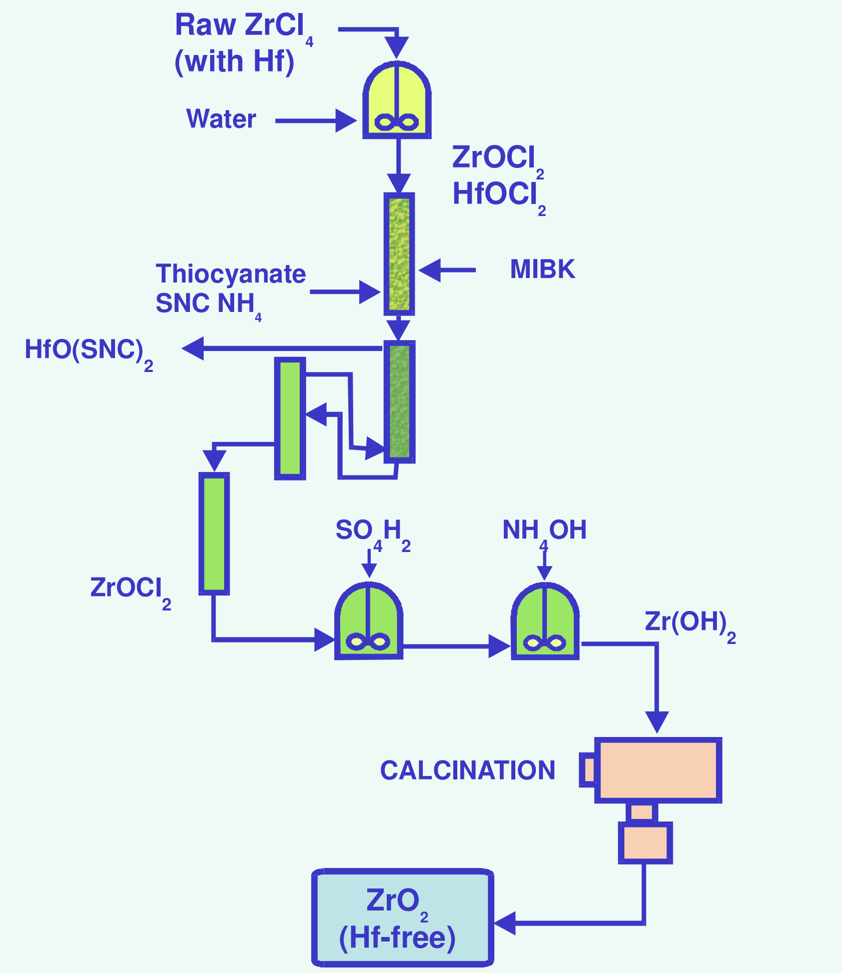
H_2SO_4

$Zr\,O\,Cl_2$
Hf < 50 ppm

$Hf\,O\,(SO_4)$
Zr < 4,5%

H. G. Weidinger

Hf-Separation by Liquid -Liquid Extraction



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-$AlCl_3$).

A solvent made of molten KCl-$AlCl_3$, is circulated from the top to the bottom (<10.000 l/h).

Vapor of $ZrCl_4$ (500℃) rises in a counterflow from bottom up.

The vapor going up is progressively enriched in $HfCl_4$.

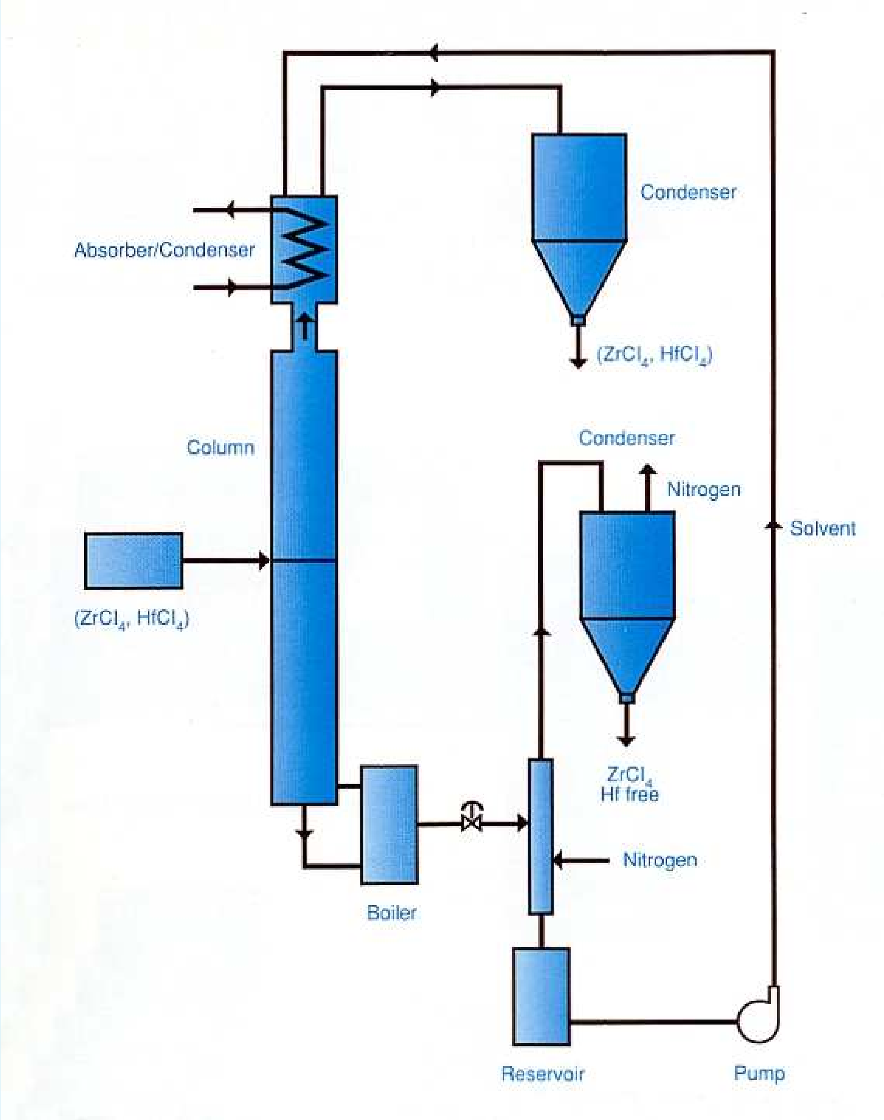
The liquid going down progressively looses Hf-content.

The $ZrCl_4$ 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



L. Moulin et al., ASTM STP 824 (1984) pp. 37-44

$ZrCl_4$ Nuclear-Grade Composition Referred to Zirconium Basis

ELEMENT	LIQUID/LIQUID DEHAFNIATION	DEHAFNIATION EXTRAC DISTILLATION
	(ppm)	(ppm)
Zn	< 120	< 120
P	< 100	< 100
Hf	30/80	35/60
Al	5/50	10/60
Na	< 50	< 50
Si	< 30	< 30
Ca, Fe, Ti	< 20	< 20
Cr, Cu, Mg, Mn, Mo, Ni, Pb, Sn, V	< 10	< 10
U	< 3	< 3
B	< 0.5	< 0.5

Moulin et.al., Zirconium in the Nuclear Industry, 6th Int’l
ASTM STP 824, 1984,

Reduction of $ZrCl_4$

Regardless which Zr/Hf separation process is used the next step in commercially producing Zr-alloys in the West is the reduction of $ZrCl_4$ to metallic Zr.

The basic chemical process is

$$ZrCl_4 + 2\,Mg \rightarrow 2MgCl_2 + Zr$$

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.

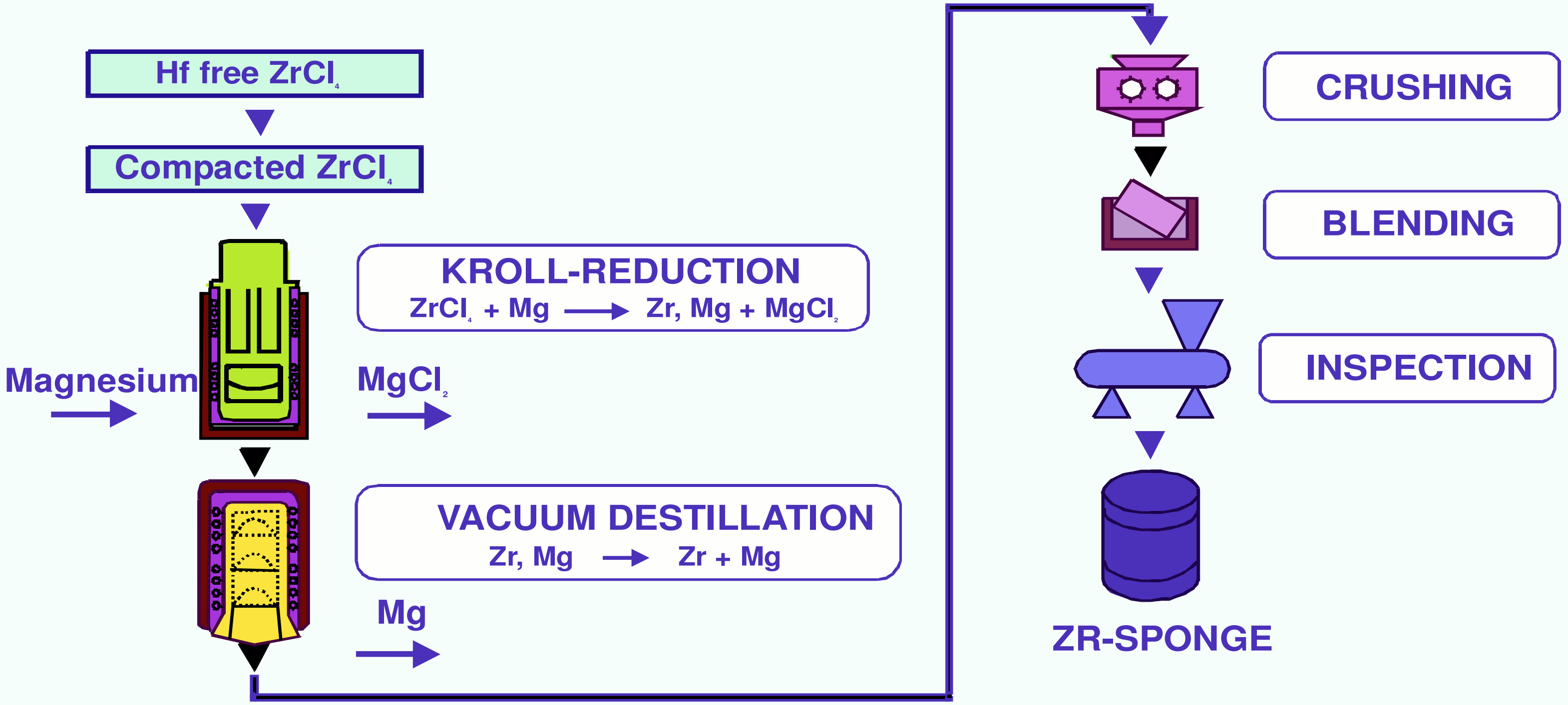
This process ends up with a very porous Zr-metal, therefore called Zr “sponge”.

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 $ZrCl_4$ by Magnesium



Hf free $ZrCl_4$

Compacted $ZrCl_4$

Magnesium

KROLL-REDUCTION

$ZrCl_4 + Mg \longrightarrow Zr, Mg + MgCl_2$

$MgCl_2$

VACUUM DESTILLATION

$Zr, Mg \longrightarrow Zr + Mg$

Mg

CRUSHING

BLENDING

INSPECTION

ZR-SPONGE

Source: Framtome-ANP

Alloying – Electrode Preparation – Melting

Due to the reactivity of the metal and its high melting temperature (1.850℃) 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.

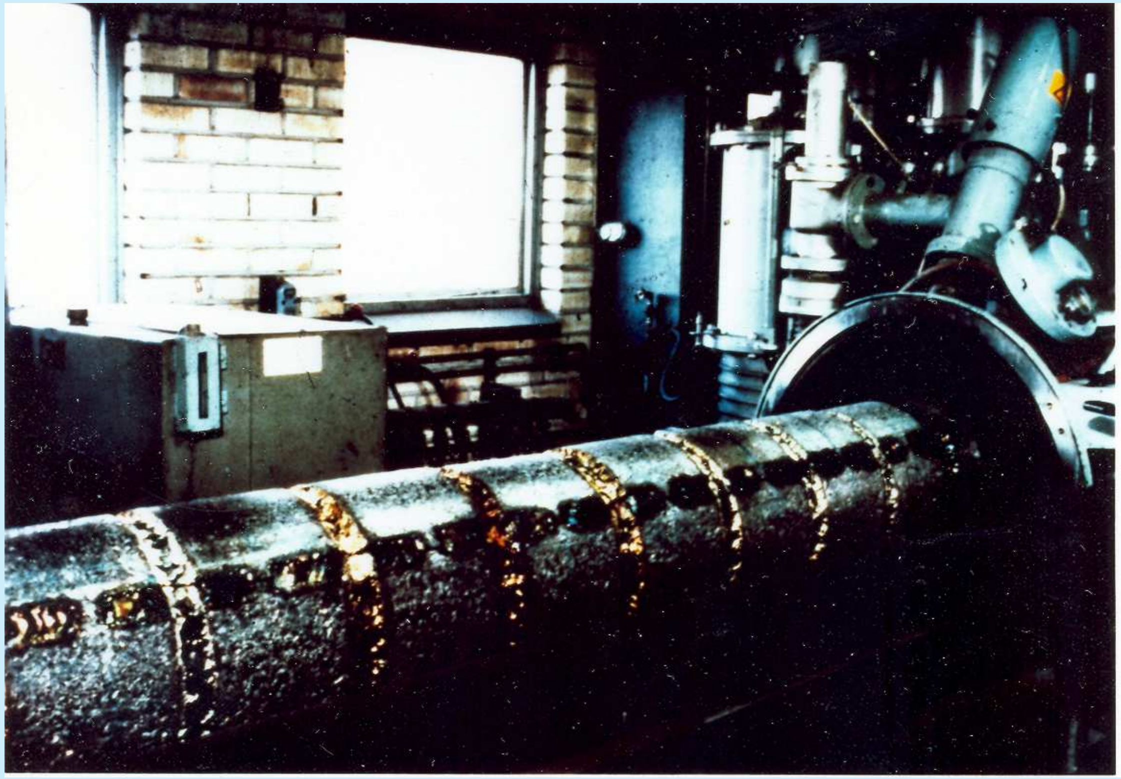
Today the ratio is much more reduced (about 25 – 30 % or less).

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



Source: Framatome-ANP

Zircaloy Electrode after Electron-Beam Welding

Melting

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

Melting temperature is 1850°C.

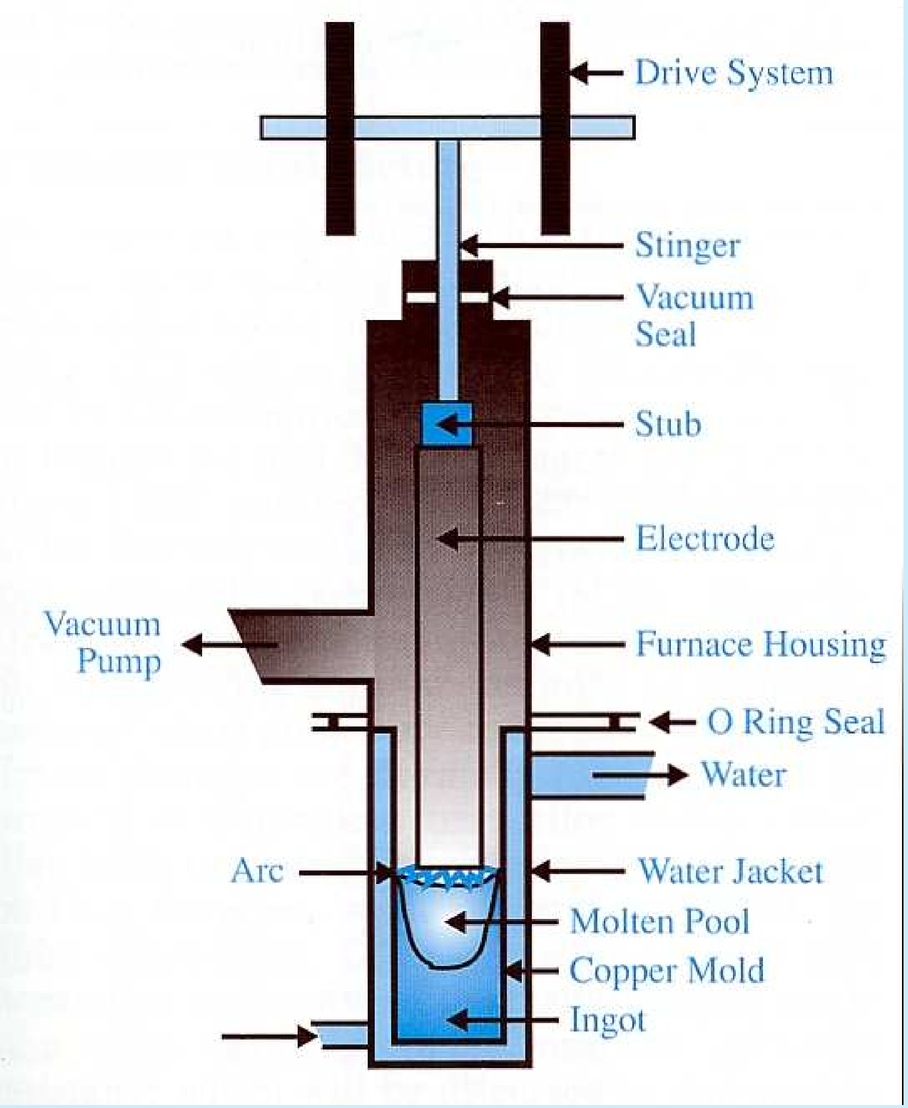
A rotating magnetic field is applied to the molten zone for improved mixing.

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.

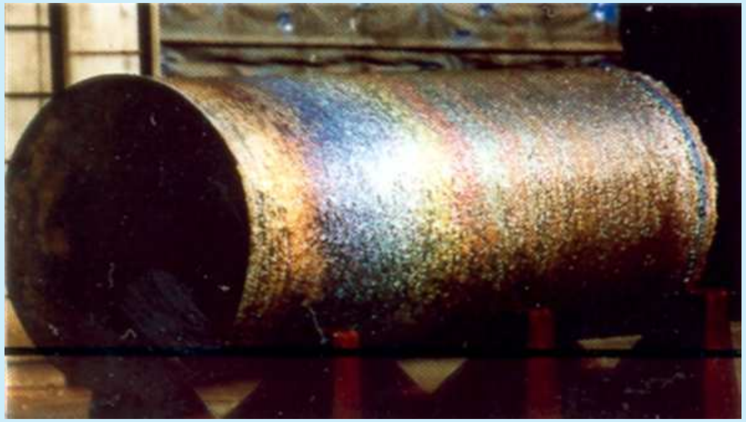
Melting requires a lot of practical experience to minimize the radial and longitudinal variation of alloying elements, since the solubility of the various elements is different in the liquid and in the solid phase.

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



Source: Framatome-ANP

6t Ingots of Zry-4, as Melted

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 α–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 β-phase temperature range (~1050℃),

  This process is used for the first steps of heavy reduction of dimensions down to octagons of ~350 mmm.

- Forging after heating into the α-phase temperature range ($\leq$ 750℃)
  This process is used for the smaller dimensions. There are two purposes for working in the α-phase temperature range:
  - breaking the fusion structure to achieve high structural homogeneity, and
  - achieving a given value for the ΣA parameter (= "cummulative annealing parameter") already in that stage of fabrication, as required by the customer. This ΣA parameter plays an important role to control the in-pile corrosion of Zircaloy (-2 and-4). In this case the β-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 α-phase temperature range.

There are very strict geometrical requirements like

straightness and wall thickness,

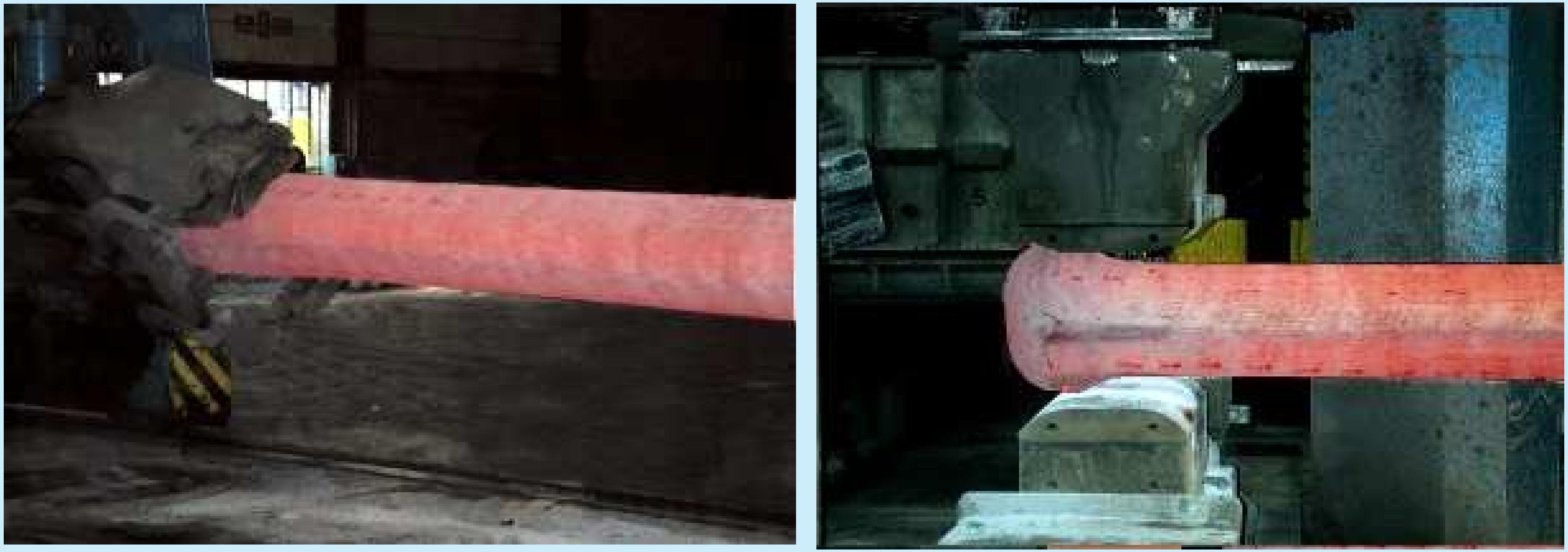
in particular with regard to concentricity,

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 Process

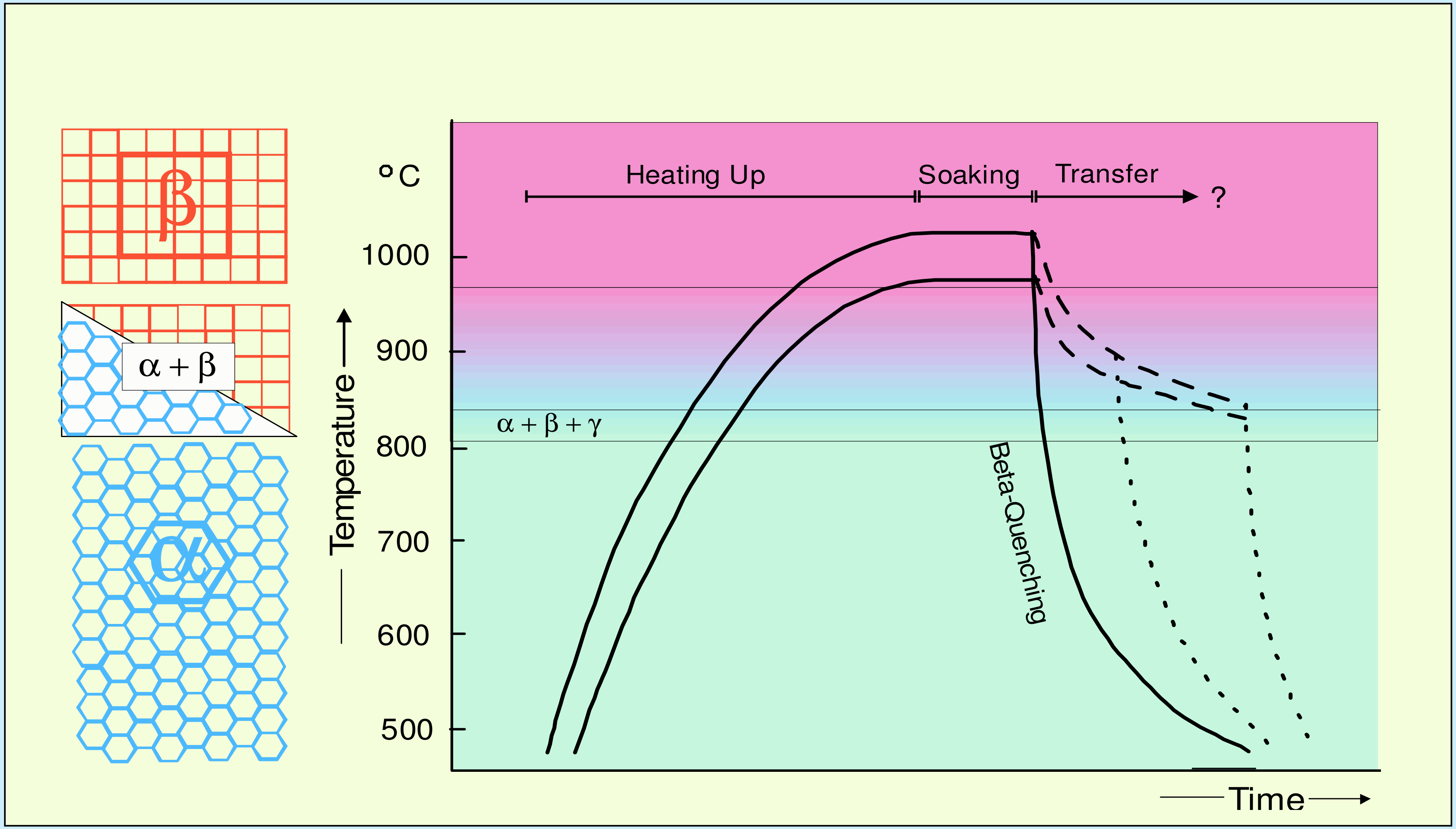
Beta-Quenching is one of the most important process steps from alloying/melting to the finish of the final product.

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℃)
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”: Δ wall-thickness : Δ 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.

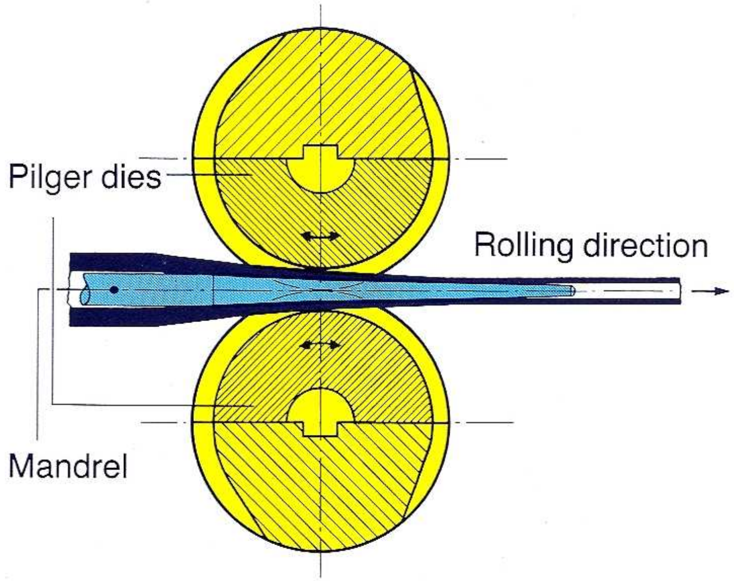
Normally an annealing procedure at ~750°C/2h is used.

Final fabrication steps are:

final annealing

finishing

Cold Deformation
Pilgering



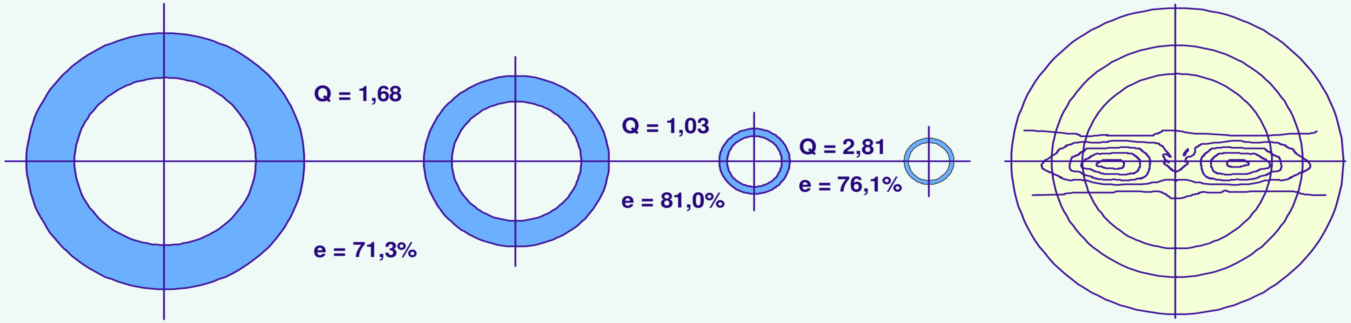
Tooling lay-out for cold pilger dies

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 Framaome-ANP/NRG

Cold Deformation Steps to Fabricate Cladding Tubes

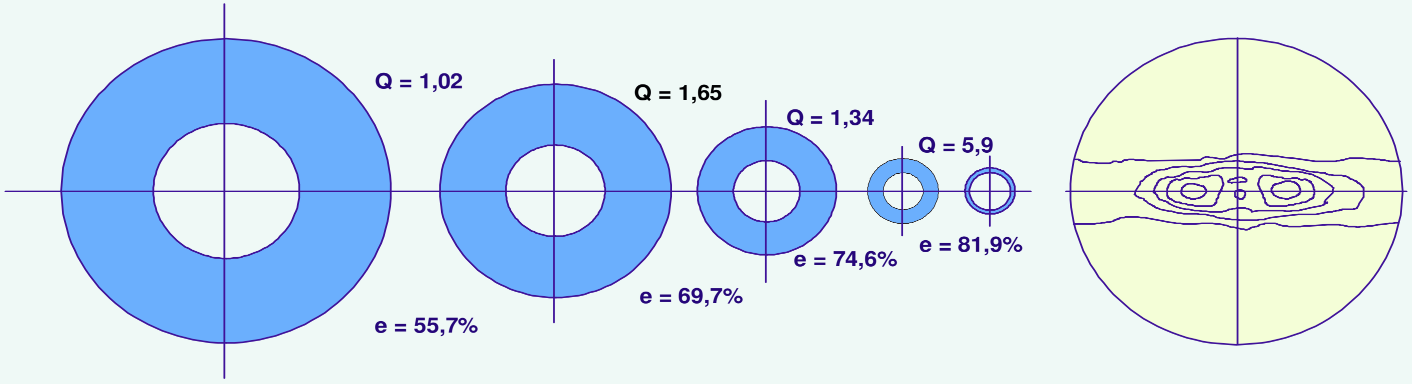
old standard fabrication PWR cladding tube



grain size

ASTM Nor. 13
4,0 µm

Texture optimized fabrication PWR cladding tube



grain size

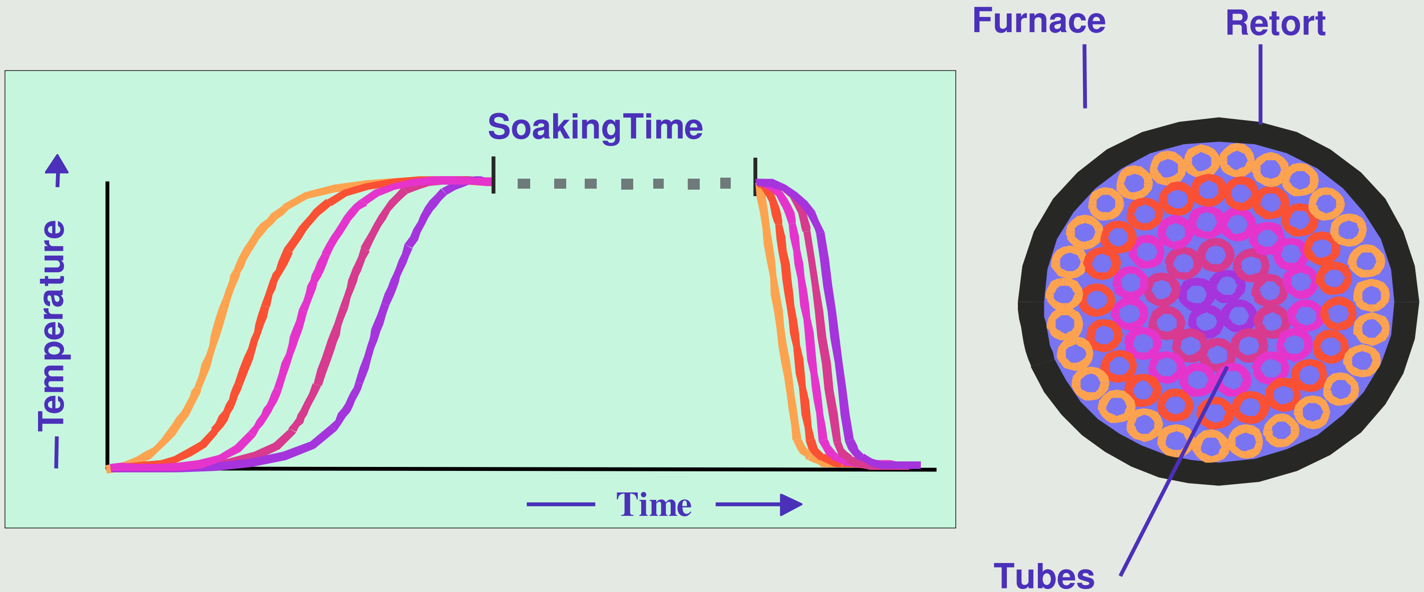
ASTM No. 13
4,0 µm

Optimizing the Texture by Modified Pilgering Sequence

M. Perez and S. Reschke; KTG Conference on Material Development for Fuel Elements in LWR, Karlsruhe, Germany (1993), p. 49 - 78

„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

Appliction

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 axia 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℃/2h is used.

Final fabrication steps are:

final annealing
finishing

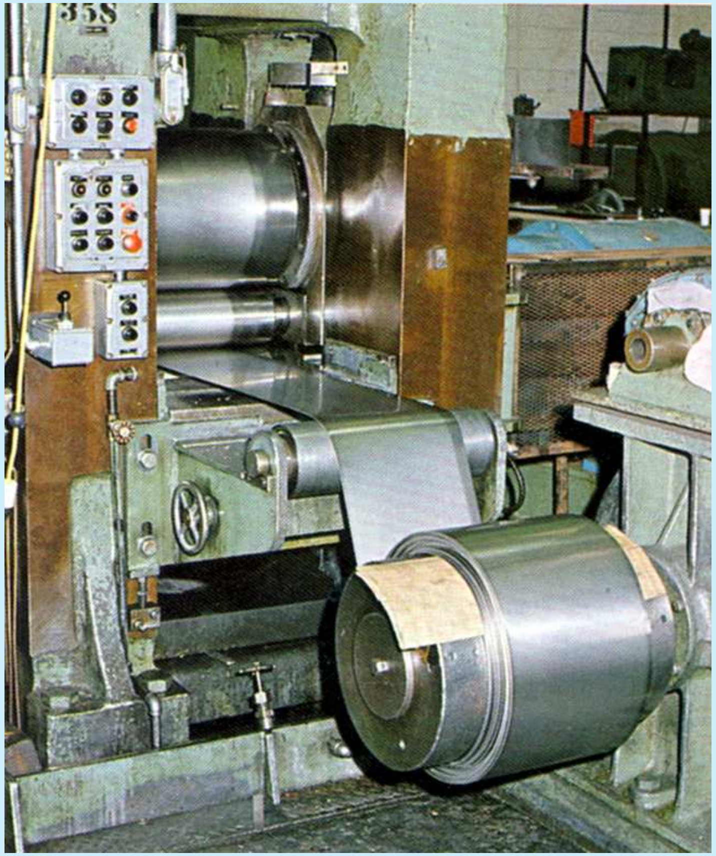
Zr-Sheet Production

- Beta-quenching of plate
- hot rolling in alpha - region
- cold rolling in several steps
- Intermediate alpha-annealing
- final alpha - anneaing
- finishing (surface)

H.G. Weidinger

Basic Process Flow Outline for
Sheet Fabrication from Beta - Quenching

Cold Rolling



Source: Wah Chang

Cold Rolling with Axial Stress