

Zirconium Alloy Fuel Clad Tubing Engineering Guide

*First Edition
December 1989*



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Acknowledgements

This Guide contains information from many sources. Those that could be referenced have been, but much of the information has been provided by members of the Sandvik Special Metals (SANDVIK) organization who have worked with zirconium products for many years. Although it is inappropriate to list all those who contributed, the following SANDVIK employees made significant contributions: Claude Stacey, Dr. Ross Bradley, Thomas Andersson, and also Craig Eucken of Teledyne Wah Chang.

A special recognition is given to John Schemel for his dedication to writing and organizing this Engineering Guide.

The data included herein is based upon the most recent information available and, to the best of our knowledge, the use of the most accurate testing equipment and techniques. Accordingly, the use or application of this data is to be understood as a basis for recommendation, but not for guarantee.

Sandvik Special Metals Corporation
Kennewick, Washington USA
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Introduction

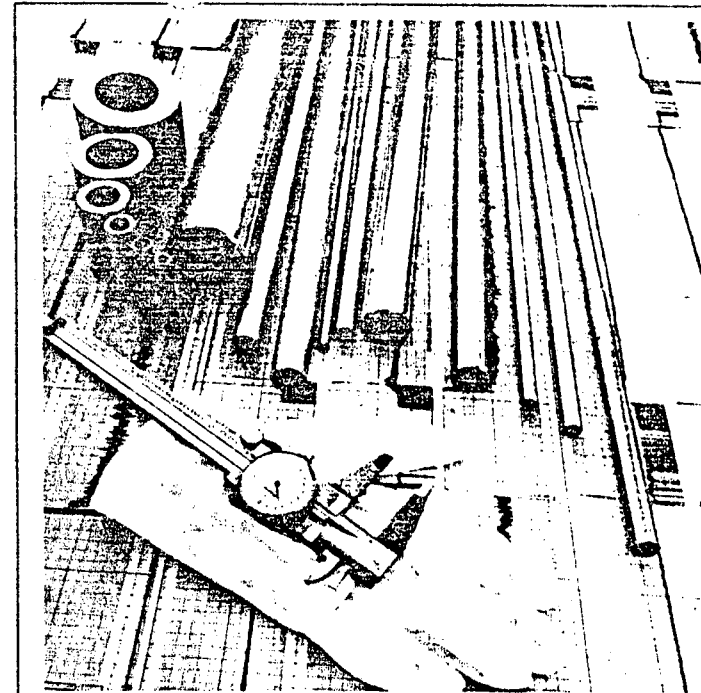
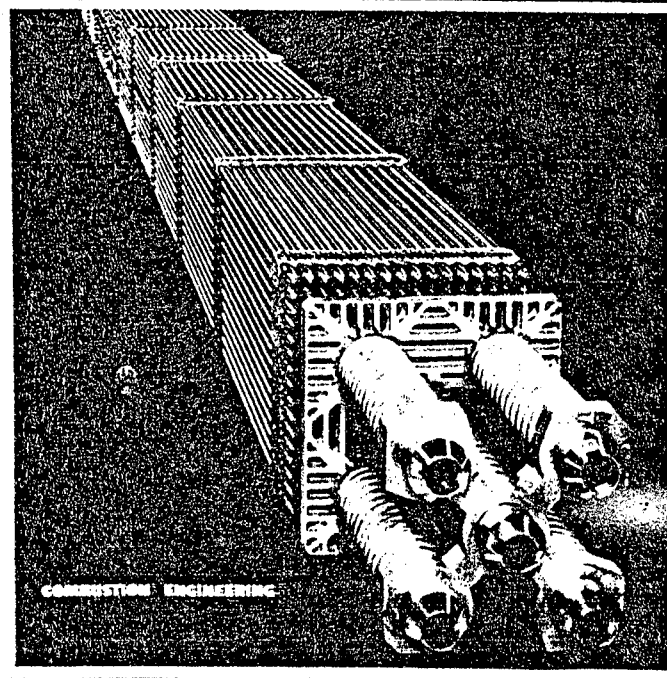
This manual has been prepared as an introduction to zircaloy fuel cladding. Its use is intended for those just becoming interested in the subject as well as a ready reference for those who routinely work with cladding. The text is general in its treatment of the subject because of the large and ever growing body of technical data that reflects the state of the art and science in 1989. Some subjects are dealt with several times so that each chapter will be reasonably complete within itself and not require constant referencing to other chapters. Each treatment will be slightly different as it comes from the perspective of the chapter. Where necessary, because of complexity or length, references to other chapters are included.

Special notation is made of processes unique to SANDVIK's way of making fuel cladding. Comparisons to conventional practice are made to assist the reader in understanding the differences and how they impact performance.

The "jargon" associated with this product is explained as each term is introduced. For instance, "zircaloy," the name was coined in the very early days at the Bettis Laboratories of the Naval Nuclear Propulsion Program and now generally represents the commercial alloys of zirconium

where tin, iron, chromium, and nickel are the major alloying elements. Zircaloy-1 was an alloy of zirconium and 2.5% tin and was never used commercially. Zircaloy-2 and -4 are in common commercial use for fuel cladding. Zircaloy-3 was a zirconium alloy containing 0.25% tin and 0.25% iron that never saw wide use, but is once again being studied. It is quite possible that the zircaloy name will continue to be extended to include all alloys with new compositions. The zirconium-1Nb alloy is often referred to as "Russian Zircaloy" since it is the standard alloy used in Russia for the same purposes as Zircaloy-2 and -4.

References listing the specific papers referred to in the text and a listing of the major sources for additional information on the subject matter covered is included in Chapter 7. The text includes specific references only where a major subject is involved to facilitate easier reading.



Chapter 1

History

While zirconium was discovered by Klaproth in 1824, our story begins in the late 1940's with the discovery that hafnium, which naturally occurs with zirconium in zircon, had caused experimenters to incorrectly calculate the thermal neutron cross section of zirconium. Researchers at Oak Ridge correctly established zirconium's cross section at 0.18 barns making it a very attractive cladding material for thermal neutron reactors.

In the early 1950's the Naval Nuclear Propulsion Program under Admiral Rickover settled on zirconium as the fuel cladding material to be used in the submarine Nautilus' water cooled reactor core. Zircaloy-2, an alloy of zirconium with tin, iron, chromium, and nickel, became the standard. It was also adopted by the engineers in Canada who were designing reactors which used natural uranium, rather than enriched uranium, for fuel. The work at Atomic Energy of Canada Ltd. (AECL) provided much of the technical data on which the commercial use of zirconium alloys was based. Unlike the Naval programs which operated under security classifications, the AECL work was widely published in open literature. Also, the Canadian work centered on tubing and commercial power reactors use tubular fuel elements.

Early U.S. power reactors used austenitic stainless steel as the fuel cladding. Chloride stress corrosion cracking of stainless steel forced the Boiling Water Reactor (BWR) engineers to shift to Zircaloy-2. Later the neutron economy of zircaloy over stainless steel made it the cladding material of choice for Pressurized Water Reactors (PWR). PWR's used a new version of zircaloy called Zircaloy-4, modified in composition to reduce the rate of absorption of hydrogen.

In Russia, an alloy of 1% niobium in zirconium became their standard for fuel cladding for both naval and commercial power reactors.

Fuel cladding for water cooled power reactors must meet a variety of technical and economic challenges. It must be corrosion resistant, have a low thermal neutron cross-section, and have satisfactory strength at the operating temperatures of the reactor core. Zircaloy met these general criteria and early fuel designs were based on the properties found in tubing produced around 1960. The push for ever more efficient fuel has been met with optimization of basic zircaloy tubing rather than a dramatic shift to another alloy system. Only the development of the Zirconium-2.5% niobium alloy for Canadian pressure tubes would lead to a new alloy; but even there, the fuel cladding remains zircaloy.

Three very significant discoveries made substantial impacts on the application of zircaloy in water-cooled reactors. The first was the discovery that nickel in Zircaloy-2 promoted absorption of hydrogen. This was very important in PWR's which use an overpressure of hydrogen in the reactor coolant which adds to hydrogen generated by the corrosion reaction. The Zircaloy-4 composition evolved with the nickel content of Zircaloy-2 being replaced with additional iron to maintain the desired corrosion resistance. The next

discovery was the effect of an intermediate "beta quench" in the manufacturing process which improved uniformity of the microstructure and reliability of the corrosion performance. Last to be discovered was the effect of metal crystal orientation on the direction in which hydrides precipitated in the tubing. Tubing made by the cold pilger or rocking process gave rise to hydride platelets that formed circumferentially around the tube leaving the tube relatively ductile. Tubing made by the drawing process commonly used for steel and other tubes produced radially oriented hydrides which made the tubing brittle. Since hydrogen was introduced into the tubing as a result of normal corrosion during service, this was an crucial effect.

There is no single set of "best" properties for a fuel clad tube. The properties must complement the requirements of the fuel design concept. The tubing manufacturer "tailor makes" the tubing to produce the properties and dimensions that provide optimum balance for each fuel design. Unfortunately, nature does not often permit one property to be set independent of the others. The attainment of a higher level in one desirable property may require some loss in another. Manufacturing parameters must therefore be adjusted to optimize the desired properties with minimum loss in other properties. For instance, it is easy to increase strength by a variety of means, but most of them drastically reduce the ductility. The means and amount of strength increase is tempered by the need to have a certain level of ductility and in no case can corrosion resistance be sacrificed. It is this complex relationship between the metal, its metallurgy, and its properties that forces a close technical relationship between fuel designers and the tube maker to get the best possible performance.

Specifications for tubing require the measurement of a number of properties essential to the design of the fuel. However, simply meeting the minimum requirements set forth in the specified properties is not sufficient to achieve optimum or, in some cases, even acceptable performance in a power reactor. In most cases, the specification for tubing includes a requirement for a process outline which defines the major process steps known to affect tube properties not easily measured by acceptance tests. The process outlines continue to evolve as new information on the process and its impact on properties and performance become known. Typically, each new tubing vendor and each major process change is subjected to an extensive qualification program to assure that the product not only meets the specification requirements, but that it also performs satisfactorily in actual service.

The sections on properties, metallurgy, manufacturing, and testing further explore the complexities of making and utilizing zirconium alloy tubing for nuclear fuel cladding.

Research and development activities are proceeding to further optimize the zircalloys as well as to develop other alloy systems. This work shows promise of even better properties to meet the challenge of more aggressive reactor environments and longer fuel residence times.

Chapter 2

Specifications

Nuclear fuel clad tubing is always procured to proprietary specifications peculiar to each fuel maker. These specifications generally follow the generic format of the American Society for Testing and Materials (ASTM) Standard for Zirconium Alloy Tubing, B353, or a new specification now being prepared specifically for fuel clad tubing. The fuel manufacturers insert additional requirements for their particular fuel design.

The "barrier clad" with its internal layer of unalloyed zirconium is not yet covered by an ASTM standard.

The ASTM standard includes methods for special tests used only for nuclear fuel cladding and universally accepted sections on referee testing, resolution of disputes, and many other such items. The main technical points covered by specifications are:

1) Composition

It is common practice for fuel designers to add several elements to the ASTM list of impurities shown in Table 2-1 to meet certain requirements based on the fuel manufacturer's past experience or the concerns of its customers. Calcium and chlorine are examples of such added impurities. It has recently become common practice to restrict

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the tin content to the lower portion of the range given in ASTM specifications for Zircaloy-4 to improve corrosion resistance and to require a maximum oxygen content different from the ASTM upper limit for either alloy.

The specific effects of the alloys and main impurity elements are covered in Chapter 5 on Metallurgy.

Table 2-1

COMPOSITION, Weight percent		
Element	Zircaloy-2 UNS R60802	Zircaloy-4 UNS R60804
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 - 0.16
Silicon	0.005 - 0.012	0.005 - 0.012
IMPURITIES, Weight percent maximum		
Aluminum	0.0075	0.0075
Boron	0.00005	0.00005
Cadmium	0.00005	0.00005
Carbon	0.0270	0.0270
Cobalt	0.0020	0.0020
Copper	0.0050	0.0050
Hafnium	0.0100	0.0100
Hydrogen	0.0025	0.0025
Magnesium	0.0020	0.0020
Manganese	0.0050	0.0050
Molybdenum	0.0050	0.0050
Nickel	---	0.0070
Nitrogen	0.0080	0.0080
Tungsten	0.010	0.010
Titanium	0.0050	0.0050
Uranium (total)	0.00035	0.00035

2) Mechanical Properties

Room temperature and elevated temperature tensile tests are normally required, but without any consensus as to the temperature of the elevated temperature test or to the levels of strength and ductility. Many specifications require an ambient temperature burst test with a minimum circumferential expansion required at the failure to demonstrate ductility. The most common test is a closed end test. Expansion in a burst test is larger in an open end test than in the closed end test and specified limits recognize this difference.

3) Corrosion Resistance

For many years a three-day test at 400C in steam was the universal acceptance test. More recently a test at about 500C to detect nodular corrosion has been added for BWR tubing.

4) Hydride Orientation

Specimens of tubing are required to be charged with hydrogen and examined to see if the resulting hydride platelets are oriented in the circumferential direction.

5) Microstructure

There is generally some sort of requirement on grain size. Direct measurement of grain size on stress relieved tubing is not possible because the grains have been elongated by the cold working. Some specifications require recrystallization of stress relieved tubing specimens in order to measure grain size.

6) Dimensions

Minimum and maximum values are given for the inside and outside diameters and length. Maximums are specified for ovality, bow, and squareness of cut. A minimum is specified for wall thickness.

7) Ultrasonic Testing

Ultrasonic testing is universally used to assure freedom from unacceptable flaws. A maximum size of a reference notch is specified.

8) Crystal Orientation

The hydride orientation test gives an indication of crystal orientation, but in some specifications a contractile strain ratio (CSR) test is also imposed.

9) Sampling Frequency

Composition, except for gases that may be absorbed during processing, is based on the analysis of the ingot from which the tubing was made. Dimensional and ultrasonic flaw testing is done in a continuous scan of each tube and other tests are generally done on two random samples from each lot of tubing.

10) Test Methods

Most testing is done to ASTM or American National Standards Institute (ANSI) standards or their counterparts in other countries. Cooperation between international standards organizations in specifying fuel cladding is one of the best examples of international technical exchange.

These tests and the details of their application are discussed in Chapter 4 on Testing and Inspection to assist engineers and quality assurance people in understanding the procedures and meaning of the results.

Some very important properties such as creep rate, long term corrosion behavior, irradiation growth, and resistance to iodine stress corrosion cracking are typical of those properties that can not be specified in the simple tests required on each lot of tubing. Most require test times that are too long for normal quality assurance testing. For these, reliance is placed on the process outline and its controls on processing.

ASTM has been a leader in providing a forum for consensus standards for fuel cladding not only in the U.S. but throughout the world. The subcommittees working on nuclear standards involving fuel cladding are:

B10.02 on Zirconium and Hafnium

G01.08 on Corrosion in Water-Cooled
Reactors

C26.02 on Fuel and Fertile Materials

E10.02 on the Behavior and Use of Metallic
Materials in Nuclear Systems

Chapter 3

Manufacture

The entire process from the ore to the tube plays a role in the performance of fuel cladding. This chapter presents background essential to understanding the metallurgical implications of the manufacturing process as well as the reasons for some of the various tests called for in the specifications. Special processing for making the barrier clad is treated in the section on extrusion and again in the discussion of beta quenching. The remaining processes are quite similar to standard cladding and the text is not complicated by mentioning all of the other considerations in making tubing from the lined extrusion.

Nearly all of the zirconium metal is extracted from zircon sand. Zircon, which is also a gem stone, is a zirconium, hafnium silicate (Zr-Hf SiO_4) with a zirconium to hafnium ratio of 50 to 1. It occurs in beach sands all over the world, but the zircon from Australia is preferred because it contains the fewest impurities that interfere with metal production. The zircon is separated from other components in the sands by a series of standard ore dressing techniques.

Sponge Manufacture

Finely ground zircon is mixed with carbon and

chlorinated to produce zirconium-hafnium tetrachloride and silicon tetrachloride. The zirconium-hafnium tetrachloride is selectively condensed and the silicon tetrachloride is sold as a by-product.

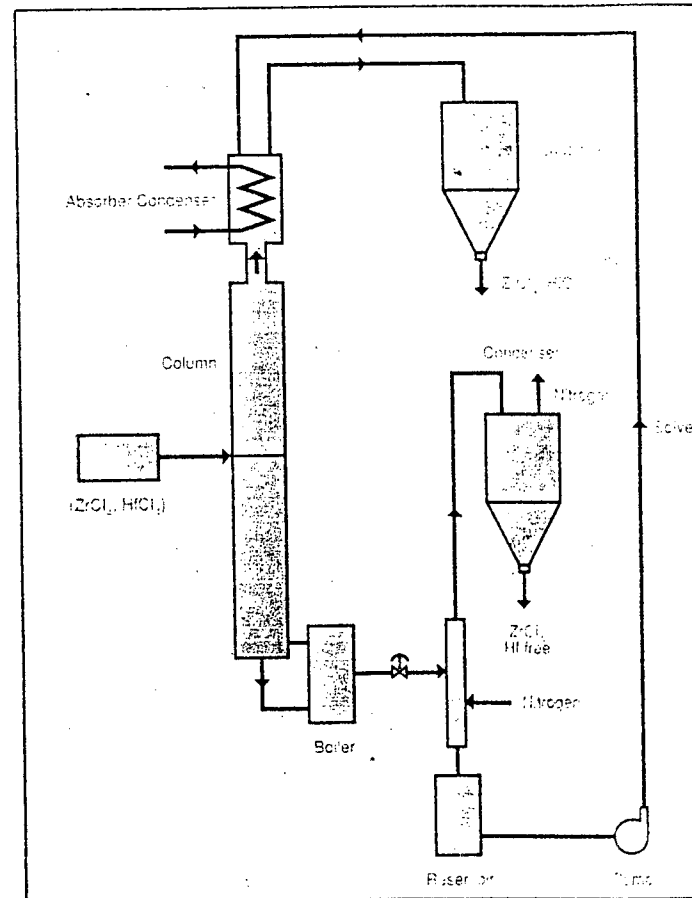
Since hafnium has a very high thermal neutron cross-section, it must be separated from the zirconium. There are two techniques used at present for this separation. The older method has been used since the 1950's and consists of dissolving the tetrachlorides in dilute hydrochloric acid, complexing the zirconium ions with ammonium thiocyanate and then extracting the hafnium with methylisobutyl ketone (MIBK) in a counter-current liquid-liquid extraction system. The aqueous phase, containing the zirconium, is mixed with sulfuric acid to precipitate the zirconium as a sulfate which is then converted to a hydroxide with ammonium hydroxide, filtered and calcined to an oxide. Most of the impurities in the zircon are taken out either in the chlorination process or the liquid-liquid extraction process so that the resulting oxide is very pure. Hafnium is stripped from the MIBK with hydrochloric acid and recovered similarly as an oxide. The zirconium oxide is then mixed with carbon and chlorinated again to produce a zirconium tetrachloride with less than 100 ppm hafnium. The zirconium tetrachloride may be further purified by sublimation or distillation from a salt solution before being reduced to metal. The process is described in detail by W.W. Stephens in ASTM STP 824 and shown in the flow sheet, Figure 3-1.

The new method of separating the hafnium from the zirconium is by distillation of hafnium tetrachloride from a potassium-aluminum chloride salt solution of the two tetrachlorides. The impurities remain in salt which is replaced at intervals. This process is described in detail by

L. Moulin et al in ASTM STP 824 and shown schematically in Figure 3-2.

In both cases, the purified zirconium tetrachloride is reduced to zirconium metal by the Kroll process using magnesium metal as the reductant. Purity of

Figure 3-2



Flow Sheet for
Hafnium
Extraction by
Distillation
from Molten
Salt

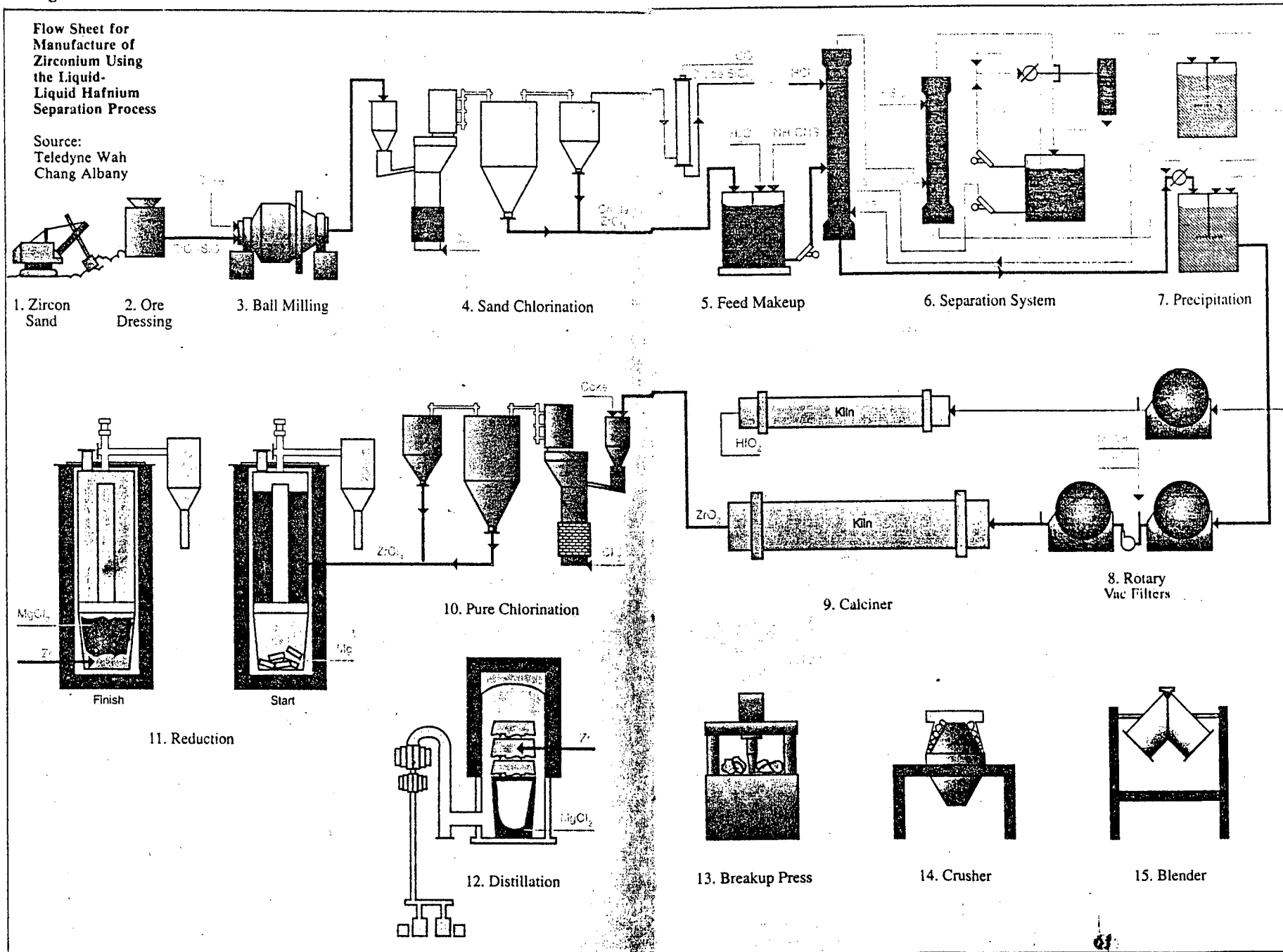
Source:
ASTM STP 824

the magnesium is very important since any impurities in the magnesium end up in the zirconium. The product of the reduction process is a mixture of zirconium metal and magnesium chloride as well as some left over magnesium metal. Most of the magnesium chloride salt is removed physically. The remaining salt, along

Figure 3-1

Flow Sheet for
Manufacture of
Zirconium Using
the Liquid-
Liquid Hafnium
Separation Process

Source:
Teledyne Wah
Chang Albany



with any residual magnesium metal, is removed by vacuum distillation at about 1000C which produces a porous zirconium mass commonly known as "sponge." The sponge from a reduction furnace load is called a "batch." Large chunks of sponge are crushed as shown in Figure 3-3, mixed, and sampled for analysis. A group of sponge batches is selected based on the analysis and combined into a "blend" which is again mixed and sampled to determine its composition. Except for a few volatile elements like chlorine and magnesium, all of the impurities present at this stage will remain with the zirconium and end up in the zircaloy. Iron, nitrogen, oxygen, and aluminum are the most common impurities present at this stage. ASTM specification, B349, covers sponge zirconium.

Figure 3-3

**Press Crushing
Zirconium
Sponge**

Source:
Teledyne Wah
Chang Albany



Ingot Manufacture

Zirconium sponge, recycle material from processing, and alloying elements are combined in various ways into an electrode for vacuum arc melting. Recycle material can be crushed, or chopped into small pieces, to be combined with the sponge and alloying elements for pressing into bri-

quettes, or it can be melted into an ingot which is then cut into slices for inclusion into the melting electrode. In both cases, extreme care is required in cleaning, sampling, and analyzing the recycle so that unwanted impurities are not introduced. Usually sponge-based briquettes and solid recycle are assembled into a long cylindrical shape and welded together as shown in Figure 3-4. Electron

Figure 3-4

**Consumable
Electrode
Showing Sponge
Compacts and
Solid Recycle
Sections**

Source:
Teledyne Wah
Chang Albany



beam welding in vacuum or plasma arc welding in an argon atmosphere is used to prevent contamination from the air. These long cylinders are about 12 to 18 inches (300 to 450 mm) in diameter and weigh a ton or more.

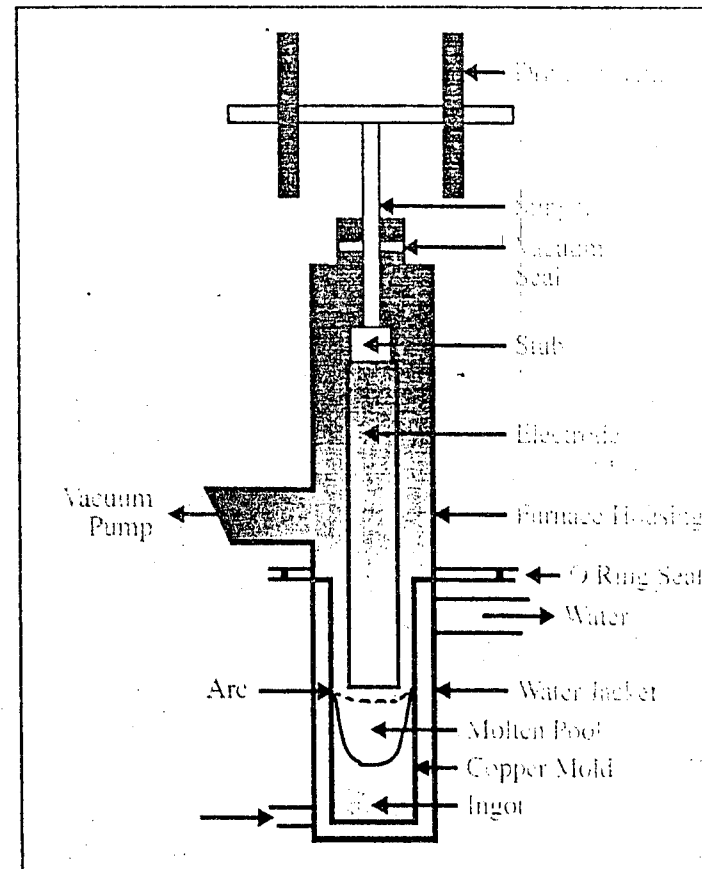
Zirconium must be melted in a vacuum or inert gas to prevent absorption of oxygen and nitrogen from the air. Consumable Electrode Vacuum Arc Melting is universally used for melting zircaloy ingots.

Zirconium, when molten, reacts with all known refractories and so it must be melted in a special way. The consumable electrode is melted into a cylindrical water cooled copper mold slightly larger than the electrode. As the arc melts the metal, a portion freezes against the cold copper mold and forms a solid layer of the zirconium alloy which acts as the container for the molten metal. The electrode is continuously consumed and the ingot builds up in the copper mold with only a portion molten at one time as shown in Figure 3-5.

Zircaloy is melted at least twice in this manner with the ingot from the first melting forming the electrode for the second melting. Much of current production is melted three times to get the best freedom from volatile elements and the most homogeneous alloy distribution. Ingots are about 30 inches (760 mm) in diameter and weigh about six tons. Since the ingot was not completely molten at one time, it is necessary to sample and analyze it at various points along its length to determine its composition. The ASTM standard calls for the first sample to be taken near the top of the ingot with additional samples taken at intervals equal to the ingot diameter down to the bottom. This recognizes that the molten pool at any time during the melting process was about one ingot diameter deep.

Figure 3-5

Pictorial Representation of Consumable Vacuum Arc Melting



Segregation is not a problem with current manufacturers as they have developed their melting techniques to produce ingots with remarkable compositional uniformity. Sampling for composition may be done under current specifications either on the ingot itself or on the material during fabrication into tubing. The sample must always be related to its position in the ingot to assure that all portions of the ingot have been analyzed. Table 3-1 shows a typical analysis report for a Zircaloy-4 ingot.

Ingots have also been tested for hardness along their length, by the Brinell method, but this practice is gradually losing significance as compositional

Table 3-1

Typical Ingot Analysis for Zircaloy-4. Sample Number 1 Represents the Top of the Ingot and Number 6 the Bottom.	Purchase Order No.:	 TELEDYNE WAH CHANG ALBANY P.O. Box 460 Albany, Oregon 97321-0136 (503) 926-4211 TWX (510) 595-0973					
	Sales Order No.:						
	Item No.:						
	Heat No.:						
	PACS No.:						
Ingot Analysis Composition: (wt. percent)							
Element:	Spec.	1	2	3	4	5	6
Sn:	1.20-1.55	1.29	1.26	1.26	1.26	1.27	1.30
Fe:	0.18-0.24	0.22	0.21	0.22	0.22	0.22	0.22
Cr:	0.07-0.13	0.12	0.11	0.11	0.11	0.12	0.11
Fe+Cr:	0.28-0.37	0.33	0.32	0.33	0.34	0.34	0.33
C:	0.0100-0.0200	0.0140	0.0140	0.0140	0.0140	0.0150	0.0140
O:	0.090-0.140	0.122	0.125	0.123	0.125	0.126	0.128
Zr:		B A L A N C E					
Ingot Analysis Impurities: (ppm)							
Element:	Spec. Max:	1	2	3	4	5	6
Al:	75	36	39	40	44	46	41
B:	0.5	< 0.2	< 0.2	< 0.2	< 0.2	0.3	< 0.2
Ca:	30	< 10	< 10	< 10	< 10	< 10	< 10
Cd:	0.5	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Cl:	20	< 5	< 5	< 5	< 5	< 5	< 5
Co:	20	< 10	< 10	< 10	< 10	< 10	< 10
Cu:	50	< 25	< 25	< 25	< 25	< 25	< 25
H:	25	< 5	< 5	< 5	< 5	< 5	< 5
Hf:	100	41	51	51	55	52	51
Mg:	20	< 10	< 10	< 10	< 10	< 10	< 10
Mn:	50	< 25	< 25	< 25	< 25	< 25	< 25
Mo:	50	< 10	< 10	< 10	< 10	< 10	< 10
N:	65	26	30	27	24	26	26
Nb:	120	< 50	< 50	< 50	< 50	< 50	< 50
Ni:	70	48	48	46	51	47	44
Pb:	130	< 25	< 25	< 25	< 25	< 25	< 25
Si:	50-120	97	93	97	100	99	93
Ta:	200	< 100	< 100	< 100	< 100	< 100	< 100
Ti:	50	< 25	< 25	< 25	< 25	< 25	< 25
U:	3.5	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
V:	50	< 25	< 25	< 25	< 25	< 25	< 25
W:	100	< 50	< 50	< 50	< 50	< 50	< 50

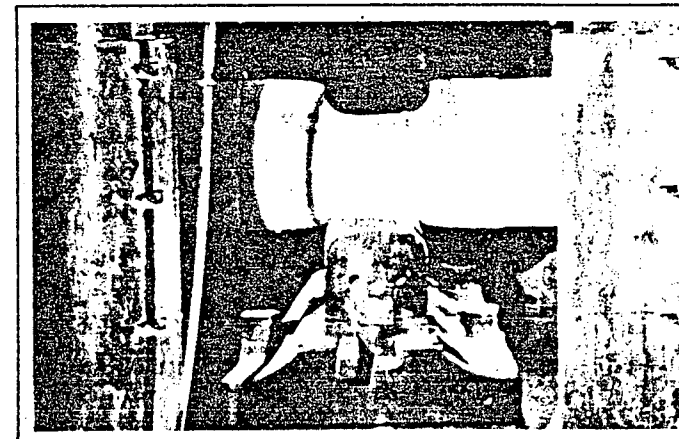
analysis has become more uniform and its effect on properties better understood. It is also common to search the ingot for solidification voids (pipe) using ultrasonic methods. This has little significance in tubing where later ultrasonic testing, that is many times more precise, is conducted on the tubing itself. Some specifications continue to require conformance to sponge and ingot specifications as well as the tubing specification. This is not necessary to assure that tubing will be satisfactory and complicates the certification of the product. The usual quality assurance

audits can demonstrate that the producers are using proper controls to assure that the process is being controlled at each manufacturing step.

Extrusion Manufacture

The ingots are made into hollow tubes by conventional metal working techniques. The ingot is made into a round bar, also call a "log", about 9 inches (225 mm) in diameter by hot forging, rolling, or a combination of these processes as shown in Figures 3-6 and 3-7. The ingots are heated to about 1100C and reduction takes place in a series of hot working steps with the workpiece being cut and reheated several times in the sequence. Heating times are normally kept as short as possible and reducing atmospheres must be avoided to prevent absorption of hydrogen. Electrically heated furnaces are normally used to avoid the problem of incomplete combustion with gas or oil that leads to hydrogen contamination. Gas- and oil-fired furnaces, when properly controlled, are quite satisfactory. Other bar sizes are also used depending on the size of the manufacturers extrusion press or to produce improved corrosion resistance which will be discussed in this chapter as well as Chapters 5 and 6.

Figure 3-6



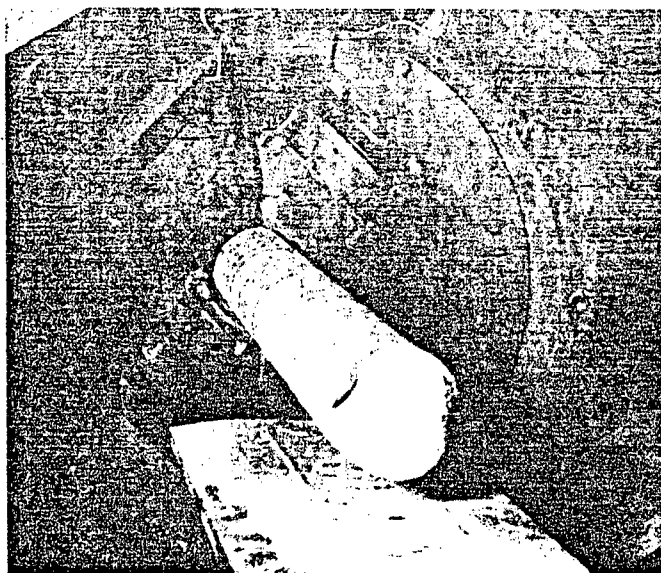
Press Forging
a Zircaloy
Ingot

Source:
Teledyne Wah
Chang Albany

Figure 3-7

Rotary Forging
Billet Stock in
a GFM Machine

Source:
Teledyne Wah
Chang Albany



This is the point in the process where the "intermediate beta quench step" mentioned in Chapter 1 is performed. Either the long bar, log, or the individual billets cut from the bar are heated into the beta phase (about 1100C) and plunged into water. Billet is the name given to the part of a bar that will be put into the extrusion press. It may still be "solid" or in some instances have the hole drilled in it prior to the quench, but generally the solid billet is heated and quenched.

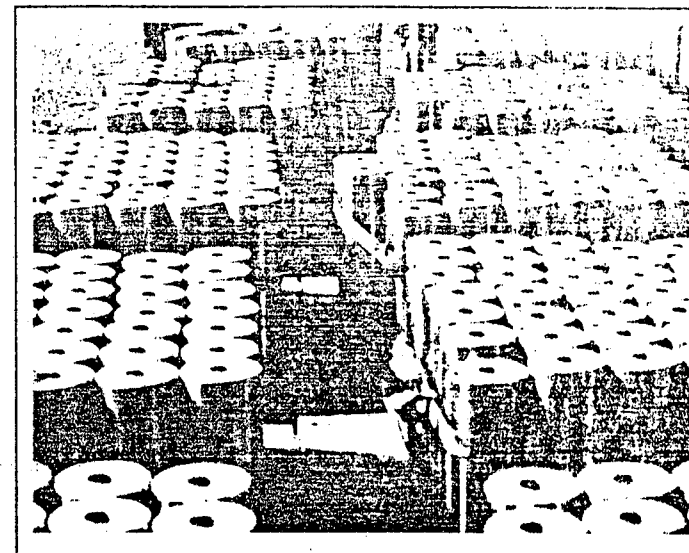
Smaller diameter billets or billets which have a hole drilled in them have faster cooling rates when quenched. In some instances the quench baths are also modified to increase the cooling rate. A faster cooling rate has been shown to be advantageous for Zircaloy-2 used in BWR cladding, but may be detrimental for Zircaloy-4 used in PWR's.

The billet is then completely machined in preparation for extrusion into a tube hollow, as shown in Figure 3-8. When "barrier clad" is to be produc-

Figure 3-8

Pallets of
Machined Billets
Ready for
Extrusion

Source:
Teledyne Wah
Chang Albany



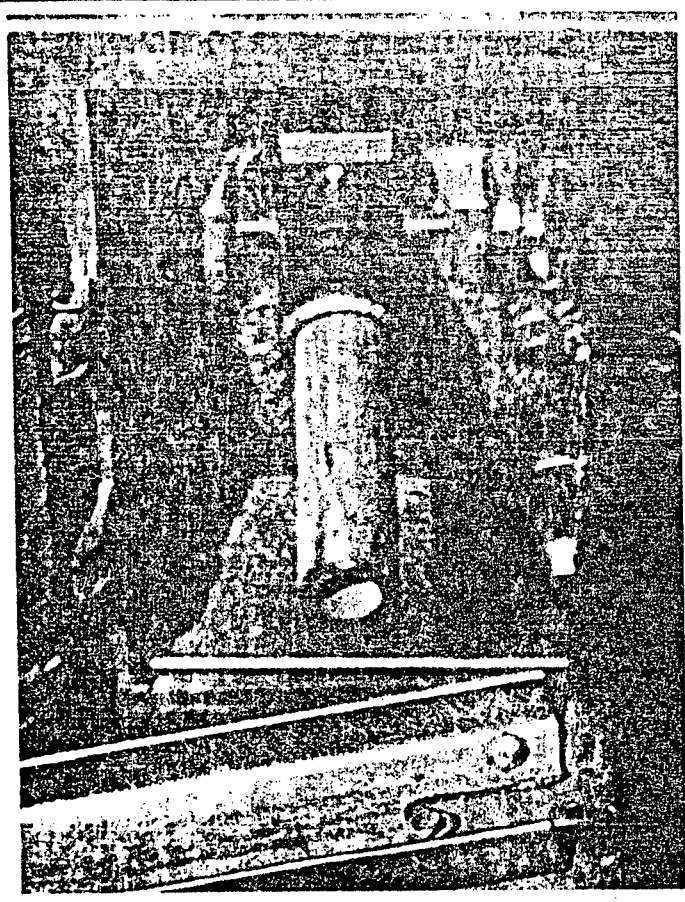
ed, the liner is inserted into the billet and welded into place using electron beam welding in a high vacuum. Cleanliness is essential in preparing the liner and the zircaloy billet so that the bond will be complete. All through the fabrication operations, each piece is carefully identified so that its position relative to the original ingot is always known. This is a most important feature of the process as it allows structural or composition problems to be traced quickly.

Zirconium tends to gall badly when it is deformed in metal working processes. It sticks to tooling and makes for poor surface quality. One way to deal with this problem in extrusion is to encase the zircaloy billet in copper which serves as a lubricant between zircaloy and tooling. Other manufacturers have developed proprietary lubrication systems that do not use metal cladding to make extrusions. Both systems are in common use as well as combinations of them. The billet is heated to about 650C and extruded to a hollow, typically about 3.4 inches (86 mm) in diameter, as shown in Figure 3-9.

Figure 3-9

Extrusion
Emerging from
an Extrusion
Press

Source:
Teledyne Wah
Chang Albany



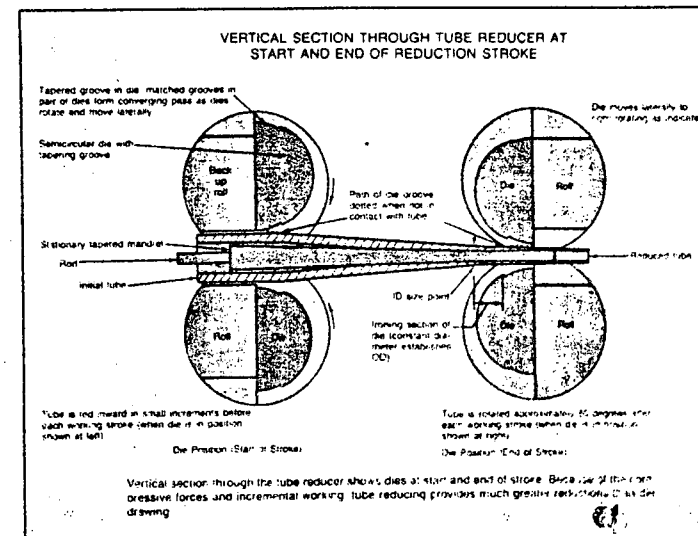
Two broad types of extrusion processes are used. The difference is in the speed of the extrusion operation. At lower speeds, the temperature changes little during the extrusion and the hollow has a cold worked structure that is best annealed prior to cold reduction. The other process uses higher extrusion speeds which increase the temperature during extrusion so that the hollow recrystallizes and an anneal is not necessary prior to cold reduction. In all cases, the temperatures are controlled so that the structure remains in the alpha phase field.

The most important points in the extrusion process are maintaining uniformity of wall thickness and concentricity, as well as good surfaces. Little can be done in the subsequent cold reductions to improve the concentricity of the tubing. Some manufacturers have developed sophisticated machines to measure and correct wall eccentricity before cold reductions are started. Inner surfaces are critical and are usually honed or broached in addition to etching in the nitric-hydrofluoric acid solution to prepare them for cold reduction. The etching solution is 15 to 30 percent nitric acid and 2 to 4 percent hydrofluoric acid. The tube hollows, either at the extruded stage or after one cold reduction, are examined ultrasonically to search for any residual flaws from the melting, forging, and extrusion operations.

Cold Pilgering

The cold reduction of the extrusion to tubing proceeds in stages called "passes." The cold reduction process is called cold pilgering, tube reducing, or rocking. All three are names for the same process as shown in Figure 3-10. In the conventional

Figure 3-10



Pictorial
Representation
of the Pilger
Tube Reduction
Process

form of this process, the tube is elongated over a tapered stationary mandrel by means of two grooved rolls, also called dies, which roll back and forth in a constant cycle. It is this motion that gave rise to the term "rocking." The roll groove is tapered and the rolls are mounted in a saddle which is moved back and forth by a crank arrangement. Gears are mounted on the machine frame so that as the saddle moves, the rolls rotate in precise relation to each other and the stationary mandrel. The ingoing tube is rotated and advanced by a small increment at the beginning of each stroke of the crank. The tube diameter and wall thickness are continuously reduced in a series of these small increments. Figure 3-11a shows the arrangement of the rolls and mandrel in a typical pilger machine. Figure 3-11b shows the hollow being reduced.

Figure 3-11a

Pilger Mill Roll Stand Showing Rolls with Tapered Groove and Tapered Mandrel in Place for Tube Reduction

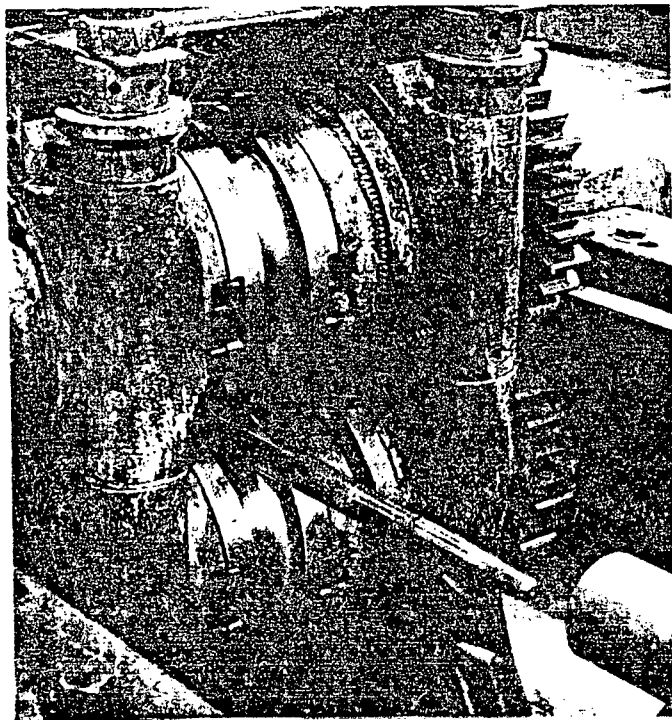
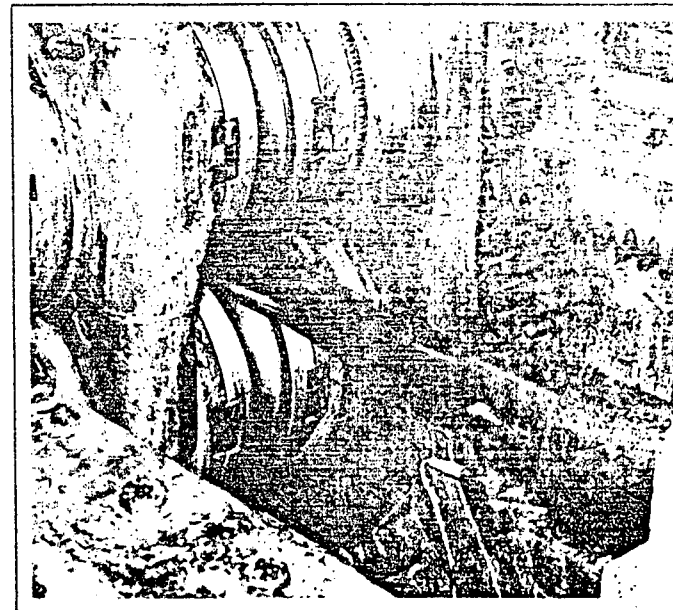


Figure 3-11b



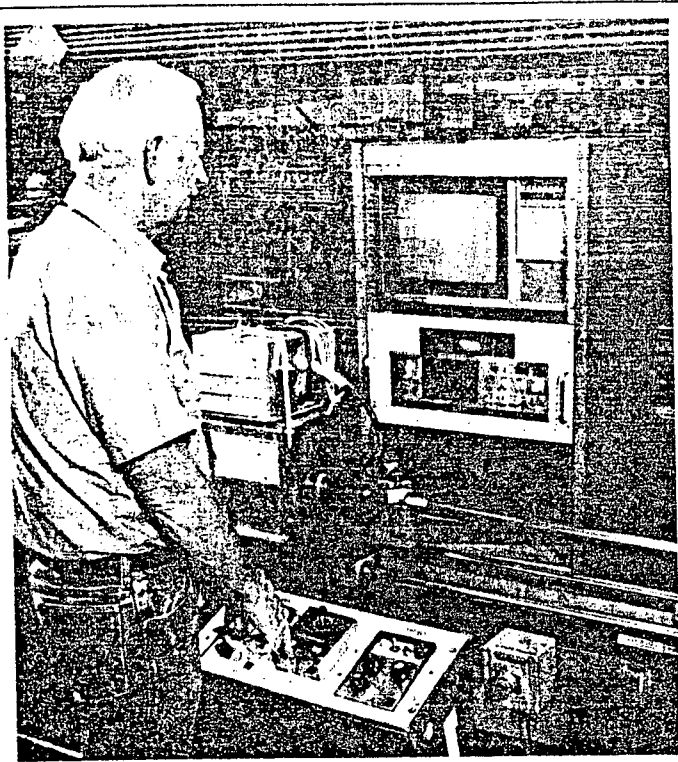
Pilger Mill with Hollow Being Reduced by Reciprocating Rolls

Each pass through the pilger machine can accomplish up to 85% reduction in cross-sectional area, although 70% is closer to the working average. About five reduction passes are required to reduce the extrusion to fuel clad tubing size. There is a special name for a tube hollow after one cold reduction pass. It is called a TREX from Tube Reduced EXtrusion. The special name was developed because this has been a common point of sale between the zirconium metal producers and the tube makers. Tube hollow is the name for any intermediate size from the extrusion down to the hollow used for the last cold reduction pass.

After each reduction pass, the zircaloy must be cleaned and annealed to prepare it for the next cold reduction. Usually there is an inspection of the surfaces (Figure 3-12) and any small tears and cracks are carefully removed so that they will not propagate in succeeding reductions.

Figure 3-12

Video Borescope
Used to Inspect
the Inner
Surface of Tubes
and Hollows



The anneals promote recrystallization and soften the hollow. The time and temperatures of these anneals have been found to play an important role in developing optimum corrosion resistance. Zircaloy-2 and Zircaloy-4 require different heat treatments to optimize corrosion because of the differences in service environments between BWR and PWR. Zircaloy-4 is annealed at a higher temperature than Zircaloy-2 for reasons explained in Chapters 5 and 6.

The actual hollow sizes used as intermediates for each size of fuel clad tubing are quite important and will be discussed in Chapter 5 on Metallurgy. Crystal orientations depend on the ratio of wall reduction to diameter reduction, and tooling must

be carefully designed to produce the desired crystal texture. SANDVIK uses conventional tool designs for most of the reductions, but differs in the way the last reduction is made. In the patented SANDVIK process, the last reduction is made on a cylindrical mandrel that advances with the hollow. Nearly all of the reduction is in the wall thickness and not in the diameter. The combination of the advancing mandrel and the relatively large wall reduction combine to produce a strongly radial crystal texture, very uniform inside diameters, and little ovality. These features are all very desirable in the fuel clad tube.

Throughout the tube making process, tubing is kept in lots. A lot is defined in all specifications as those tubes made by the same process from a single ingot and given the final heat treatment in a single furnace load. SANDVIK goes further and keeps tube lots related to their position in the original ingot so that any composition variation will not cause variation in response to the heat treatment.

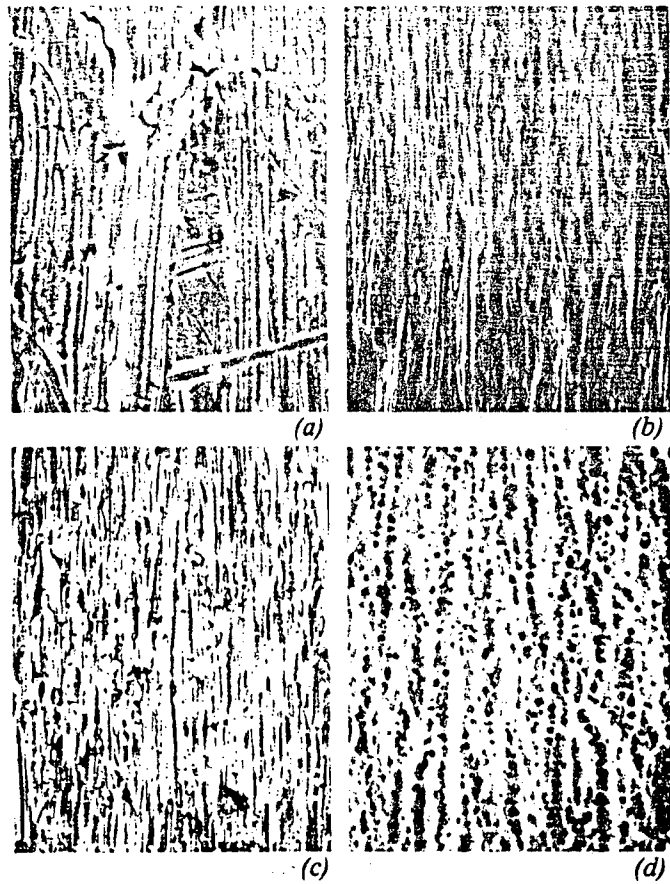
Tube Finishing

After the last cold reduction, the tubing must be heat treated to produce the desired mechanical properties and the surfaces prepared to give the desired finish. SANDVIK pioneered a flowing nitric-hydrofluoric acid etch with a proprietary rinsing system that produces a very smooth inner surface with a minimum of residual fluoride on it as shown in Figure 3-13. As explained later, this finish provides better resistance to iodine stress corrosion cracking than other finishes, such as grit blasted or dip etched, which are also commonly applied to cladding tubes. SANDVIK also employs furnaces for the final heat treatment that are uniform within about 1 degree Celsius so that mechanical properties are extremely uniform within each tube lot and between lots. After the final heat treatment, the tubing is straightened,

Figure 3-13

Comparison of
Inner Surfaces
of Tubing:

- a) As Pilgered
- b) SANDVIK
Proprietary
Flowing
Acid Etch
- c) Grit Blasted
- d) Conventional
Dip Etch



belt polished on the outer surface to remove all traces of the old metal surface, and cleaned again prior to inspection. Silicon carbide abrasives are used since they cut cleanly and do not load up with zirconium metal causing the surfaces to smear.

The real difference in tubing is not only the differences cited in the description of the manufacturing steps, but in the uniformity and care with which they are carried out. There is indeed a difference that cannot be expressed in specifications or process outlines. THAT DIFFERENCE means reliability in performance.

Chapter 4

Testing and Inspection

This chapter covers the tests and inspections usually applied to zircaloy fuel clad tubing with some background as to what the test or inspection is expected to show and where it originated. Unusual aspects of test methods are explained.

Composition

The samples used to represent the composition of metal products are taken from the parent "heat" or melt. In the case of zircaloy the "heat" is an ingot. A single sample will not suffice for a consumable electrode arc melted zircaloy ingot since only a portion of it is molten at any one time. The molten pool is about one ingot diameter in depth; therefore, the sampling plan calls for one sample to be taken near the top of the ingot and then additional samples to be taken each ingot diameter down the ingot. The sample for analysis requires both a solid portion for oxygen and hydrogen determination as well as turnings for other analysis. The samples can be obtained from the sidewall of the ingot or from a slice of the product either in its final form or part way through the manufacturing process. For tubing, some manufacturers take the sample slices when the forged bar is cut up to make the extrusion billets.

Customarily, the manufacturer's ingot analysis forms a part of the tube maker's product certification. A typical ingot analysis certificate is shown in Table 3-1. Hydrogen and oxygen can be added to zircaloy during hot working or heat treating if proper procedures are not observed. Specifications require that a sample for hydrogen and oxygen be taken from finished tubing. Many specifications also require nitrogen analysis on a sample of finished tubing.

Nitrogen is not absorbed during the manufacturing process and need not be required to be analyzed on samples from the the tubing.

Optical Emission Spectroscopy

An electric discharge is used to excite the sample, producing light which can be broken down into spectral lines representing the elements present in the sample. Each element has a group of characteristic wavelengths of light which it emits when excited. The intensity of a specific line for each element is measured either on a photographic plate or by a phototube to determine concentration.

A metal sample may be excited directly by the electric discharge in a technique called "point-to-plane." Alternately, turnings may be burned to oxide and the oxide packed into an electrode and excited by the electric discharge. This technique is called "carrier distillation."

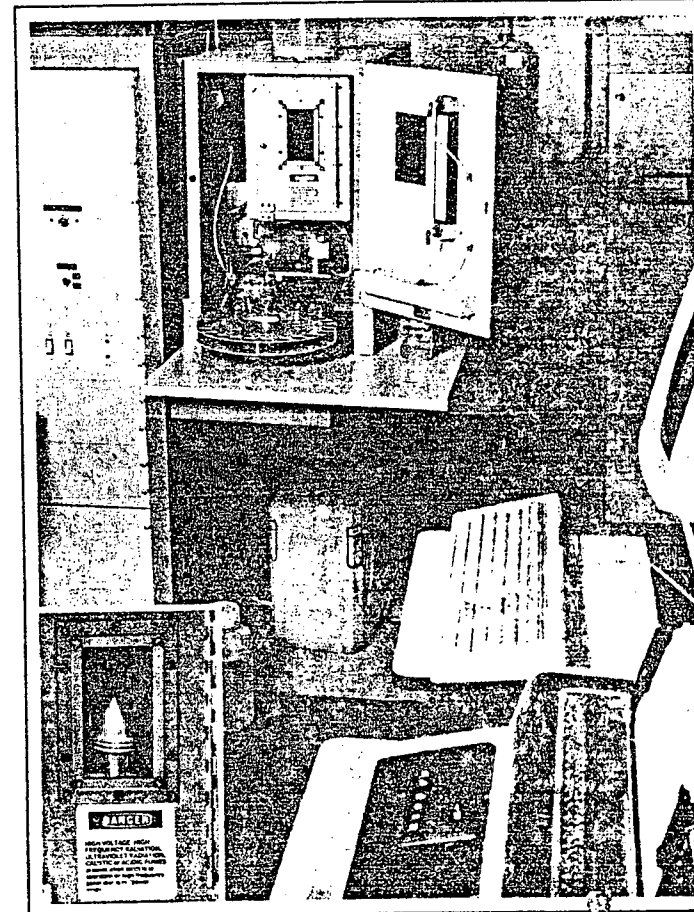
Standards of known concentration are used to construct curves of intensity vs. concentration for each element. Samples of previously analyzed material are run intermittently with the unknown samples as a check on calibration.

Plasma Emission Spectroscopy

Inductively Coupled Plasma (ICP) and Direct Current Plasma (DCP) techniques utilize an argon

gas plasma to excite sample solutions for spectrographic analysis as shown in Figure 4-1. To date, this technique has been used in determination of concentrations of 25 elements in zirconium and its alloys. Aluminum, calcium, cobalt, chromium, copper, iron, hafnium, magnesium, manganese, molybdenum, sodium, niobium, phosphorus, silicon, tin, tantalum, and zinc can be determined directly from a dissolved sample. Analysis for boron, cadmium, lead, and uranium require that the sample solution be concentrated before being fed to the plasma for analysis.

Figure 4-1



Apparatus
for Induction
Coupled Plasma
Spectrography

Source: AB
Sandvik Steel

A metal sample is dissolved in a nitric-hydrofluoric acid solution and diluted to a specific volume. The solution is then drawn into the argon plasma running at 7000 to 15000C where it is excited. The light emitted is broken down into spectral lines and the analysis made in the same fashion as for optical emission spectrography. The use of solutions for the analysis makes the preparation of comparative standards more precise than is possible in the optical spectrographic technique.

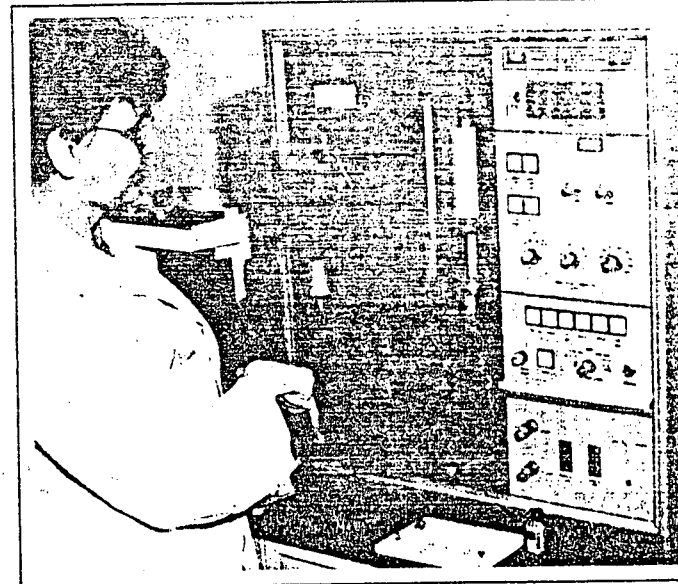
Atomic Absorption Spectrophotometry

Like plasma emission spectroscopy, atomic absorption techniques use a solution of the sample for the analysis. The technique differs in that only one element can be determined at a time and the measurement is of absorbed rather than emitted light. The principle of the method is that unexcited atoms of an element absorb the radiation emitted by that same element when excited. A hollow cathode discharge tube of the desired element provides a source of the radiation and the atoms of the element in the sample solution are dispersed in a flame between the hollow cathode tube and a detector. The amount of a specific wavelength of light that is absorbed is proportional to the amount of the element present in the sample.

Inert Gas Fusion

Oxygen, nitrogen, and hydrogen can be determined by variations of this technique using equipment such as shown in Figure 4-2. A metal sample is fused at high temperature in a graphite crucible using a metal flux and the resulting gases are swept into an analytical instrument by an inert carrier gas. The gases are purified by passing through various scrubber columns and then isolated by gas chromatography. The concentration of the gas to

Figure 4-2



Impulse Fusion Apparatus for Determination of Oxygen

be measured is then determined by a thermistor bridge and displayed on a digital voltmeter.

If only oxygen is to be determined, a nickel flux is used. If both oxygen and nitrogen are to be determined from the same sample, platinum is used as the flux and the carrier gas is very high purity helium.

Hydrogen determinations use tin as the flux and argon as the carrier gas. Hydrogen can also be measured by vacuum extracting the gas from the sample without melting it and measuring the hydrogen gas volumetrically.

Kjeldahl Method for Nitrogen

The metal sample is dissolved in a hydrofluoric-hydrochloric acid mixture. Sodium hydroxide is then added to the solution until the solution becomes basic and the nitrogen is converted to ammonium ion. Ammonia is driven from the solution by steam distillation and collected in

another solution. The nitrogen can then be determined either by titrating the solution with boric acid or colorimetrically. For the latter technique, Nessler's reagent is added to develop a yellow color. The intensity of the color is proportional to the nitrogen content and is measured in a spectrophotometer.

Carbon Analysis

Carbon is determined by fusing the sample in a ceramic crucible using a tin flux in the presence of oxygen. The carbon dioxide thus formed is measured either by a thermistor bridge or an infrared detector.

Fluorimetric Analysis for Uranium

Uranium compounds will fluoresce when exposed to ultraviolet light. For small concentrations, the intensity of the fluorescence is proportional to the uranium concentration. Because the concentration of uranium in zircaloy is so small, the solution of the sample must be concentrated before the fluorescence technique can be used. The uranium is extracted from the acid solution using MIBK. A sample of the MIBK solution containing the uranium is then absorbed in a sodium-lithium fluoride pellet. The fluorescence of the pellet in a fluorimeter yields the measure of uranium in the original sample.

The analytical techniques vary from laboratory to laboratory depending on the equipment available and the number of samples run each day. Samples of known composition are interspersed with the unknown in all of the analytical techniques to assure that calibration is maintained.

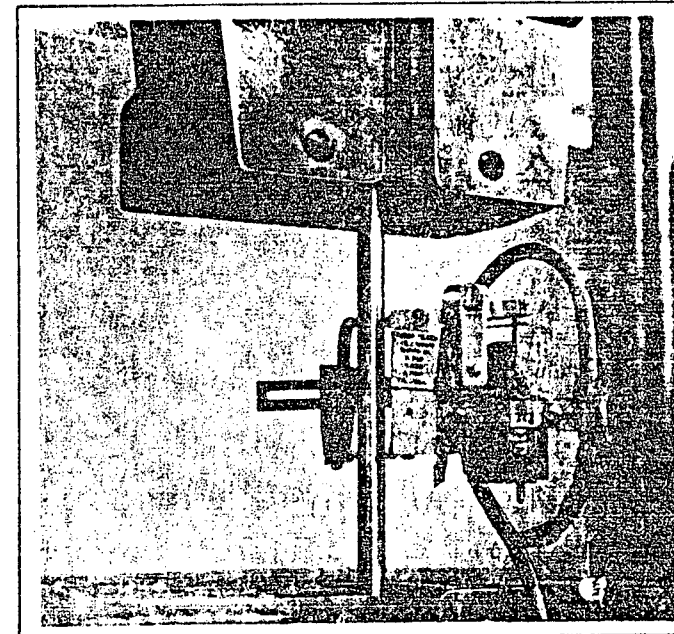
ASTM for the most part has not been able to remain current in the analytical methods as they have been evolving quite rapidly as new equipment

became available. It is generally accepted that each manufacturer's methods are acceptable subject to the quality assurance audits which require demonstration that the methods are traceable to some satisfactory standard. The National Bureau of Standards has not been able to completely meet the need for standards and other avenues are generally a part of each laboratory's calibration system.

Tensile Testing

Tensile tests, usually at both room temperature and at some temperature near 370C, are performed according to ASTM methods. Method E8 is used for room temperature testing and E21 for elevated temperature testing. Zircaloy is strain rate sensitive and thus, its yield strength will rise with increasing rate of strain. ASTM and other zircaloy specifications require that the strain rate be controlled at levels where the expected variations will have little effect on the measured values. The full tube cross section is tested as shown in Figure 4-3. SANDVIK uses

Figure 4-3



Tension Test
Showing
Extensometer
for Measuring
Elongation
Under Loading

weight and length to calculate the cross sectional area because the measurement of weight is about ten times more accurate than the measurement of wall thickness in determining the cross sectional area. Stress relieved zircaloy tubing does not exhibit a nice linear relationship between stress and strain even in the elastic region. Consequently, the determination of the 0.2% offset yield strength is not as precise as it is for most other metals because the offset must be drawn from a curve rather than a straight line on the stress strain plot.

Burst Test

There are many factors affecting the internal pressure burst test and the measurement of the resulting circumferential elongation. These were studied extensively by an ASTM round-robin program and reported in ASTM STP 551. The recommendations of this work were embodied in the Appendix to the ASTM tubing specification covering the burst test method. The rate of pressurization, the amount of stored energy in the system, and the clearance between the tube and the internal mandrel all have significant effects on the circumferential elongation at the burst. A photograph of a typical burst test sample is shown in Figure 4-4.

Contractile Strain Ratio (CSR)

This test, originated by Westinghouse in the late 1960's, is a measure of crystal orientation. It consists of carefully measuring the diameter of the tube at set locations and measuring the distance between a series of scribe marks about one-half inch apart along the tube. The tube is then strained about 4% in tension and measurements repeated. The changes in diameter and length make possible the calculation of the ratio of circumferential strain to wall thickness strain which is the CSR value. Values less than one indicate a

Figure 4-4



Specimen After Testing Showing Expansion Prior to Burst

circumferential crystal texture and values of two or more indicate a highly radial texture. Some investigators have used the failed tensile specimens for measurements, but this is not correct since with large strains there is a rotation of the crystals during deformation which leads to incorrect estimates of the initial texture of the tube.

The precision with which the diameter and length change measurements are made determines the accuracy of the test. Specially designed equipment is necessary for these measurements since the changes are very small. Normal measurements with hand held micrometers and ruled scales will not suffice.

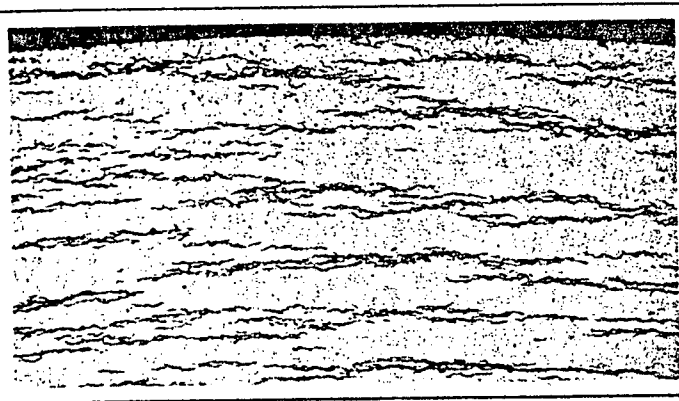
Hydride Orientation

Since highly circumferential hydride platelets are necessary for good ductility after corrosion in reactor service, a test to look at this feature was developed. The test method is also an Appendix to the ASTM tubing specification. A small tube sample must be carefully cut to avoid adding a residual stress to the sample because stress affects the direction of hydride precipitation. The sample is charged with about 200 ppm hydrogen by one of the methods listed in the ASTM specification. SANDVIK uses the gas hydriding method. The sample must be slowly cooled from about 350C in order for the hydride platelets to be large enough to count accurately. The sample is mounted using a cold epoxy type mounting, again to avoid stress and heat which would redissolve the hydrides. The sample is then given a normal metallographic polish and a light etch to bring out the hydride platelets as shown in Figure 4-5. Hydride platelets

Figure 4-5

Micrograph of Typical SANDVIK Tubing Showing the Circumferential Hydrides.

$f_h < 0.1$.
Bright Field, 200x



with angles smaller than some specified value, usually 40 degrees to the radial direction, are classified as radial and the others as circumferential. The ratio of radial platelets to total platelets is the hydride fraction known as f_h . The usual specified value for stress relieved tubing is 0.3. SANDVIK typically has values smaller than 0.1 and uses a comparative micrograph for the determination rather than the tedious counting technique.

Corrosion Testing

The universal test for corrosion resistance has been the 72 hour test in 400C steam. The test method is ASTM Method G2. For fuel clad tubing, which is generally furnished with an etched inner surface and a belt ground outer surface, the test is performed on the tubing as manufactured rather than being etched in the laboratory prior to testing as the ASTM test method describes. This utilizes the test for both basic corrosion resistance and to prove freedom of the tubing from surface contamination that might adversely affect corrosion resistance.

The specimens oxidize during the test, forming an adherent hard black oxide on the etched inner surface. The belt ground outer surface has a grey appearance because of the roughness introduced by the grinding which leaves tiny zircaloy particles on the surface. These particles form a white oxide with an underlying black oxide giving the specimen a grey appearance. Criteria for acceptance is a maximum gain in weight (22 mg/sq dm for the 3-day, 400C steam test) and a visual examination of the oxide film. Visual standards are generally used to evaluate both inner and outer surfaces for both the proper corrosion film and any evidence of residual contaminants. Fluoride from the etching is the most common surface contaminant and it shows up as a pale bluish stain. While undesirable, the fluoride stains do not result in any increase in corrosion beyond the

initial few days in a test. The protective black oxide forms under the stain and it vanishes as the oxide film grows thicker with time.

More recently, a test using etched specimens and a test temperature of 500 to 520C has been used for Zircaloy-2 when applied in BWR's. This test shows the tendency of the tubing to be susceptible to nodular corrosion. ASTM has been working for several years to obtain consensus on a reproducible test method, but as yet has not been able to do so. The test is extremely sensitive to the test temperature. Variations in test temperature considered normal in the 400C test are too great for the higher temperature test, if results are to be reproducible. The results of the ASTM work are reported in ASTM STP 939.

Surface Roughness

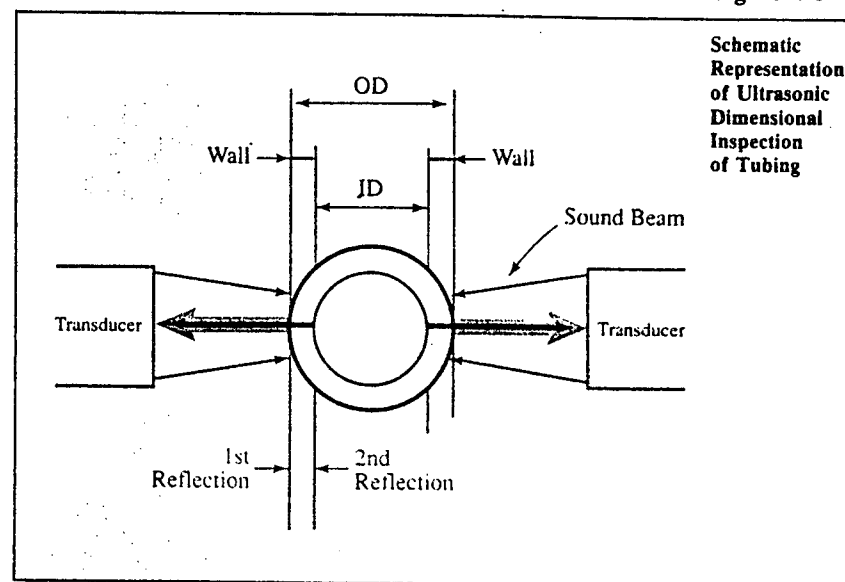
Most specifications specify a maximum roughness using the ANSI profilometer method of measurement. Here a diamond stylus, with a certain radius, is moved over the surface and the deviation from a plane is measured. The arithmetic average of the deviation is calculated by the instrument and expressed in microinches or micrometers. This is the common method used for many machined and ground parts of all kinds. When evaluating the surface of zircaloy fuel cladding, the features making up the deviations from the plane can be quite different and still produce the same numerical value. A mechanically polished, an etched, or a grit blasted surface can all have the same roughness value and yet respond much differently to important tests. EPRI, in report NP3009, showed that the iodine stress corrosion cracking tendencies were markedly different for a rocked, etched, and grit blasted surfaces even though the tubes had much the same roughness when measured by the profilometer technique. Figure 3-13 from Chapter 3 shows these surfaces

in scanning electron microscope photographs. Even etched surfaces can be quite different. The flowing acid etch used by SANDVIK produces much smoother surfaces than does the simple dip etch in common use.

Dimensional Inspection

Ultrasonics makes possible inspection of tubing along its entire length for diameter and wall thickness. In this technique, two transducers are positioned on either side of the tube in a water tank as shown in Figure 4-6. A sound beam is sent toward the tube from each transducer. The first reflection from each sound beam is from the outer surface of the tube and is used to measure the outside diameter. The sound beams then enter the tube from each side and return a second reflection from the inner tube surface that is used to measure the wall thickness. The inside diameter is determined by electronically subtracting the two wall thicknesses from the outside diameter. The measurements are made several thousand times a

Figure 4-6



second as the tube is rotated and advanced through the transducers. The measurements are displayed either on a paper chart or a cathode ray tube (CRT) with the recording made on magnetic media. SANDVIK's equipment marks with an ink spray any part of a tube that does not meet the acceptance criteria. The test systems are calibrated with carefully made dimensional standards which are run through the tester at frequent intervals to assure that the test remains accurate. Air gauging and laser micrometers are other methods that are more precise than the ultrasonic test and are used to confirm measurements when tubes approach the specified limits. These more precise methods are used to establish the reference values for the tube type dimensional standards used in the ultrasonic dimensional inspection. The air gauge and laser micrometer can be set up with standards directly traceable to NBS.

Ultrasonic
Inspection
Equipment for
Dimensional
and Flaw
Inspections



0.0015" x 25.4mm = 3/16"
0.0062" x 25.4mm = 1/58" approx
0.004" x 25.4mm = 10/128"

Ultrasonic Flaw Testing

This test is a very precise version of a test widely used for other, more common, types of tubing. To reliably test using the small artificial reference defects specified for fuel clad tubing, requires a special technique that was codified by ASTM and listed in the Appendix to the fuel cladding specification. Typically, notches 0.0015 inch deep, 0.004 inch wide and 0.062 inch long are made by electric discharge machining in the tube standard. Four notches are used; one oriented axially and one circumferentially, on each the inner and outer surfaces. Four transducers are positioned so that the tube being tested is searched axially in both directions and circumferentially in both directions. Any tube that returns a signal equal to or greater than that returned by the standard notch is considered unacceptable. Most manufacturers set their equipment to indicate a flaw at a somewhat smaller signal level than that returned by the specified notch so that there is no possibility that the tube, upon retesting with a slightly different test sensitivity, will not pass the test. It is not possible to have all four of the flaw indications from the standard notches equal, so the reject level is based on the smallest of the four.

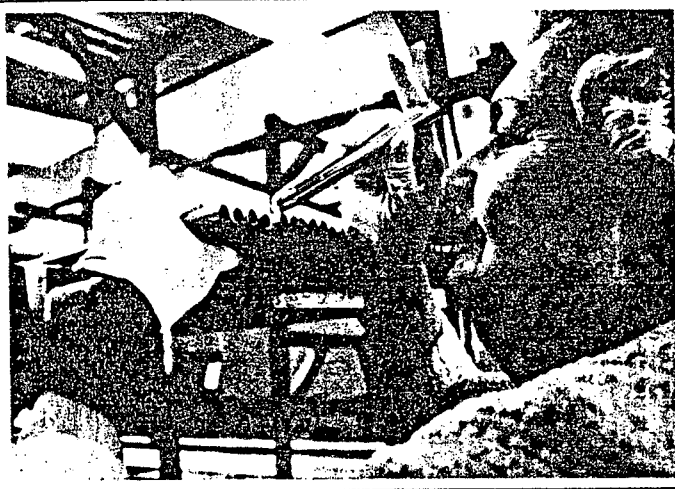
It is important to note that the test measures the amplitude of sound reflected from the standard notch and is not strictly measuring flaw depth. This is a common misconception that leads to serious misunderstanding of the test results. The indication is more closely a measure of the projected area of the notch than its depth.

Visual Inspection

Just as the name indicates, this is a visual inspection by a person using the unaided eye. Ordinarily, no magnification is used. Under strong lighting, the tubes are examined for flaws on the

outer surface by rolling groups of them back and forth. The eye picks up differences and calls attention to flaws, contamination, or other features that deviate from the uniform finish of the tubing. The inner surfaces are inspected by looking down the tube from each end against a fluorescent lamp. By bending the tube slightly, the inner surface can be clearly seen for about two feet and large flaws or dirt can be seen anywhere in the tube. Indications visible to the eye are judged against standards of acceptability. Where necessary, magnification or the use of a borescope is employed to make a final judgment.

Visual Inspection
of the Inner
Surface of
the Tubing



Chapter 5

Metallurgy

Metallurgical phenomena play a very significant role in the production and performance of zircaloy fuel clad tubing. Very strong anisotropy results from the hexagonal crystal structure and a characteristic preferred crystal orientation in tubing. The microstructure consists of intermetallic compound particles dispersed in a basic structure of alpha zirconium. The size, composition, and distribution of this compound phase has a profound effect on nearly all of the properties of interest for fuel cladding.

Zircaloy-2 and Zircaloy-4 were long thought to be nearly identical in metallurgy and properties, except that Zircaloy-4 absorbed less of the hydrogen produced by the corrosion reaction in water or steam. It is now known that while there are many similarities between the two alloys, there are differences that are crucial to their application in power reactors.

This section presents a basic review of the metallurgical phenomena that are important in understanding how the composition of the alloys and their metallurgical structures act to produce the properties observed in the tubing. The discussion is not exhaustive in detail, but is intended for engineers not already familiar with the basic

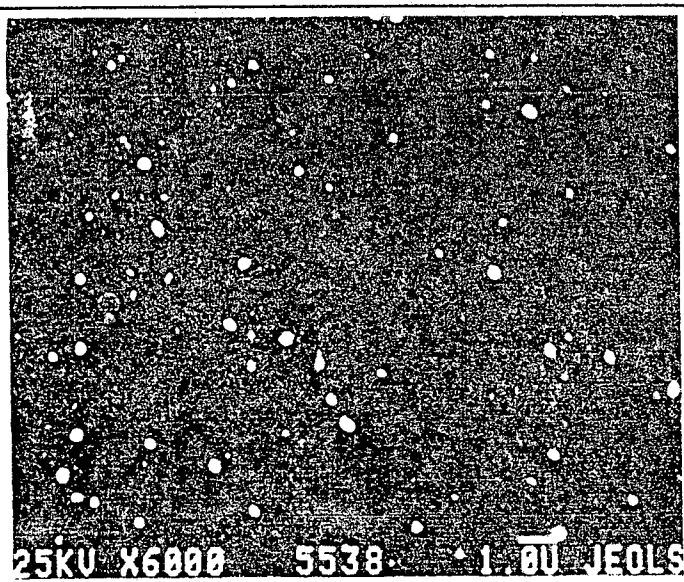
metallurgy of these very interesting alloys. There is much yet to be learned as there are some phenomena that have not been satisfactorily explained.

Microstructures

Both Zircaloy-2 and -4 have recrystallized microstructures at room temperature that consist of equiaxed grains of alpha zirconium with tin in solid solution and the iron, chromium, and nickel forming intermetallic compounds with zirconium. These intermetallic compounds appear as particles in the microstructure as shown in Figure 5-1. The primary intermetallic compound particles are the $ZrCr_2$ and Zr_2Ni type compounds with iron replacing some of the chromium or nickel. Both compounds are found in Zircaloy-2, while only the chromium compound is found in Zircaloy-4. In spite of the larger content of iron in the alloys, the zirconium-iron compounds are not normally present.

Figure 5-1

Scanning
Electron
Micrograph of
Recrystallized
Zircaloy
Showing
Distribution of
Intermetallic
Compound
Particles



The alpha or room temperature phase is hexagonal close-packed (HCP). The beta phase is body centered cubic (BCC) and begins to form at the grain boundaries of the alpha grains upon heating above about 800C. The fraction of beta phase increases with temperature until at about 980C the microstructure is all beta phase and nearly all of the alloying elements are in solid solution. The beta phase cannot be retained at room temperature even by rapid quenching. The rate of cooling from the beta phase is one of the most significant parameters with respect to corrosion resistance.

Alloys

Some elements such as carbon, oxygen, and silicon were originally considered to be impurities in zircaloy. They have now been found to be essential alloying elements that play an important role in the metallurgy of the alloys.

The elements in zircaloy that tend to stabilize the alpha phase are tin, oxygen, hafnium, aluminum, and nitrogen. Antimony, beryllium, lead, and cadmium are also alpha stabilizing elements.

Iron, chromium, nickel, molybdenum, copper, niobium, tantalum, vanadium, thorium, uranium, tungsten, titanium, manganese, cobalt, and silver all are beta stabilizing elements that lower the allotropic transformation temperature and usually form eutectics at higher concentrations and intermetallic compounds at room temperature.

Tin

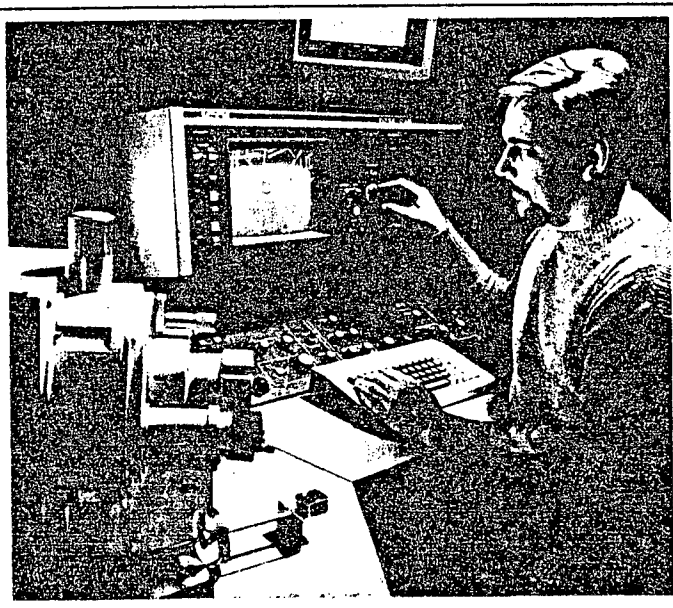
Tin is the original alloying element in the zircaloy family. Zircaloy-1 was simply zirconium with 2.5% tin. Tin is an alpha stabilizing element that exists in solid solution in zircaloy contrary to the phase diagrams which show solid solubilities less than the 1.5% in Zircaloy-2 and -4. Tin was added

to counteract the adverse effects of the relatively high nitrogen content of early zirconium on corrosion resistance. In addition, it significantly strengthens the alloy. With the current low levels of nitrogen present in zirconium, only 0.2% tin would be needed to tie up the nitrogen. In the recrystallized condition, the tin and oxygen contents determine the strength levels.

Iron, Chromium, and Nickel

These elements promote the corrosion resistance of the alloy in a yet-to-be understood manner. They are beta stabilizers and rapidly dissolve in the beta phase as it forms on heating above 800C. They are mobile in the alpha phase above about 600C so that intermetallic particle size and distribution can change markedly depending on the thermal history of the tubing. Prolonged heating, just below the start of the beta phase transformation, will lead to the intermetallic particles precipitating at the grain boundaries.

Examination of
Zircaloy
Specimens for
Intermetallic
Particles in
the Scanning
Electron
Microscope



Nickel was found to promote the absorption of hydrogen during corrosion in water and steam. Zircaloy-4 was developed by eliminating the nickel, but required additional iron in place of the nickel to get good corrosion resistance. The roles of these alloying elements in the corrosion mechanisms is the focus of much of the research being conducted to improve corrosion resistance.

Oxygen

This was one of the first impurities to become an alloying element in zircaloy. Oxygen is an alpha stabilizer and is soluble in both alpha and beta zirconium well above the levels used in commercial alloys. It functions as a solid solution strengthener in zircaloy and is generally present at about 0.125% in fuel clad tubing. Its strengthening effect is greater at room temperature than at elevated temperatures.

Carbon

Another impurity turned alloying element, carbon is soluble in alpha zirconium to about 100 ppm and only sparingly soluble in beta zirconium. It forms an extremely stable zirconium carbide which seems to nucleate the beta phase upon heating and the alpha phase upon quenching. In both cases, carbon plays a critical role in developing the desired morphology during beta heat treatments. Its presence seems to promote the basket weave type morphology instead of the parallel plate morphology. Carbon that is in solid solution adds some strength to the alloy. At contents greater than 250 ppm, carbide particles are clearly visible in the optical microscope. SANDVIK uses a carbon level of about 120 ppm to produce a desirable microstructure in billets and extrusions. Some investigators have claimed an adverse effect of carbon on corrosion resistance, but as yet the evidence is not convincing.

Silicon

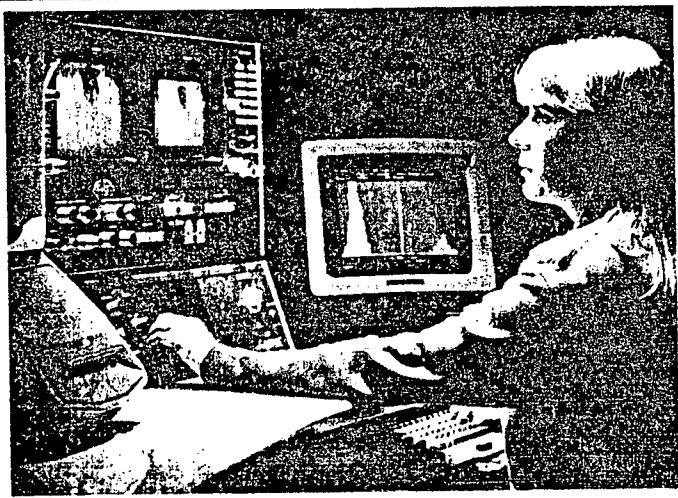
Like carbon, silicon is not very soluble in beta or alpha zirconium and plays a similar role in nucleating the phases during beta heat treatments. This results in a finer beta grain size and improved corrosion resistance. SANDVIK uses about 80 ppm silicon in its zircalloys.

Impurities

The list of impurities given in various specifications come from a variety of sources, not all of which are technically valid. A listing of the more commonly referenced impurities, with some discussion of their effect and where the requirement might have originated, is presented next.

1. Elements known to have an adverse effect on corrosion behavior such as aluminum and nitrogen.
2. Elements with high thermal neutron cross sections such as hafnium, boron, cadmium, and molybdenum.
3. Other elements that could be introduced during manufacture.

Examination of
Zircaloy in
the Electron
Microscope



- a. Lead - At one time, the Kroll reduction furnaces had lead seals which were solidified during the evacuation step where air was removed from the furnace and molten during the reduction cycle so that a rapid rise in internal pressure would not explode the unit. If the vessel developed a negative pressure during the reduction cycle, the lead was sucked into the furnace, contaminating the zirconium.
- b. Copper - The ingots are melted in a water-cooled copper mold and a displaced arc during melting can lead to copper contamination in the ingot, or at least on its surface. In actual fact, copper, to the level of several hundred parts per million, improves the corrosion resistance of zircaloy.
- c. Magnesium - Magnesium is the metal used to reduce zirconium from the tetrachloride in the Kroll process. Most of the magnesium is removed during vacuum distillation of the zirconium sponge. The remainder is removed during the vacuum melting. The requirement probably originated when inert gas melting was used in the early production years.
- d. Hydrogen - Hydrogen is reduced to about 5 ppm during vacuum arc melting, but can be picked up from the atmosphere during heating operations or from the hydrogen produced during pickling operations, if not done properly. The nitric acid in the nitric-hydrofluoric acid mixture used for pickling zircaloy oxidizes the hydrogen and prevents its absorption into the metal. Vacuum annealing in the alpha phase range at pressures of 5×10^{-5} torr or less will reduce the hydrogen content to less than 25 ppm if higher levels are introduced during manufacturing. Hydrogen is not very soluble in zirconium at room temperature and

precipitates in the form of zirconium hydride platelets preferentially at right angles to the basal pole of the metal crystal. Small hydrides are visible even at hydrogen levels as low as 15 ppm.

Most impurities listed are generally not present in nuclear grade zirconium and for practical purposes are reported as less than half the specified limit. Measurable levels of hafnium, nitrogen, aluminum, and hydrogen are normally found, but are generally well below specified limits. Table 3-1, in Chapter 3, shows a typical composition certification for an ingot.

Beta Quenching

In the 1960's, a manufacturing process consisting of a solution anneal in the beta phase above 1000C followed by a water quench at some intermediate size during manufacture became standard practice. This heat treatment is commonly called "beta quenching." In the tubing manufacturing sequence, the forged bars are beta quenched prior to extrusion or, in some instances, prior to the last hot working step. The beta phase is not retained at room temperature, but transforms to alpha plus the intermetallic compound particles during the quench.

The beta quenched structure is shown in Figure 5-2a and 5-2b and is known as the "Widmannstätten" structure. Two variations of this structure can occur. One is the basket weave variation shown in Figure 5-2a. The other is a parallel plate structure, where the platelets are lined up with each other and have the same crystal orientation as shown in Figure 5-2b. In this form, the prior beta grain containing the parallel plates reacts to working like a large single grain. The basket weave structure is much preferred for uniform deformation during cold working. Both the basket weave and the

Figure 5-2a



Micrograph
Showing
"Basket Weave"
Structure
Resulting from
Beta Quench

Polarized
Light 150x

Figure 5-2b



Micrograph
Showing
"Parallel Plate"
Structure
Resulting from
Beta Quench

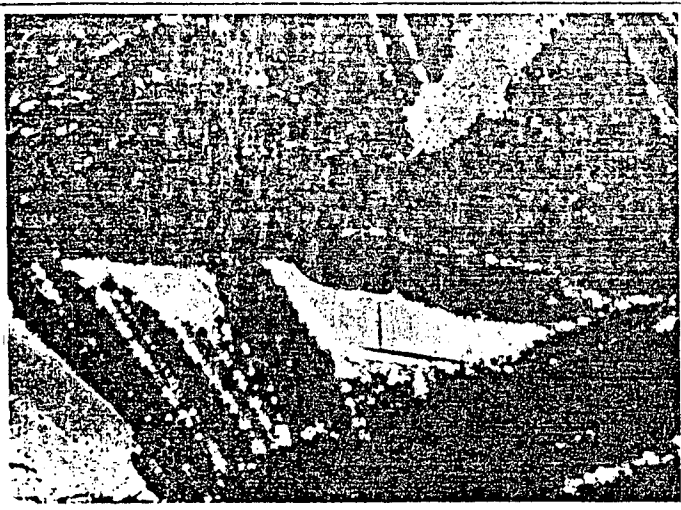
Polarized
Light 150x

parallel plate structures consist of alpha zirconium platelets with fine particles of intermetallic compounds, some of which are metastable, at the platelet boundaries as shown in Figure 5-3. There is also some evidence from work on corrosion in sulfuric acid that there is a thin continuous film at the platelet boundaries. The particle size and

Figure 5-3

Micrograph
Showing
Intermetallic
Compound
Particles of
the Platelet
Boundaries of
the Beta
Quenched
Structure

Polarized
Light 625x



platelet width are related to the quench rate. The size and shape of the parent beta grains are easily seen in low magnification micrographs like Figure 5-4.

Figure 5-4

Micrograph
Showing
Prior Beta
Grain Shape in
Beta Quenched
Structure

Polarized
Light 115x



The reason for the heat treatment is to refine the size of the intermetallic particles, since the slow cooling encountered in the ingot forging steps leads to large particles grouped along grain boundaries. This structure is not very corrosion resistant and does not completely break up during subsequent metal working operations, regardless of the deformation temperature. A cooling rate of 50°C/min is sufficient to refine the particle size and distribution for good corrosion resistance to 400C steam. Faster rates may be better for nodular corrosion resistance, but a specific minimum rate has not yet been established. Smaller diameter billets, or billets with the hole drilled in them prior to the beta quench, have been used to obtain more rapid quench rates.

In 1975, SANDVIK developed and patented a process for tubing that incorporated a second beta quench step during the series of cold reductions used to make tubing. This process produced Zircaloy-2 tubing with remarkable resistance to nodular corrosion, while retaining the structure and mechanical properties of cold worked and stress relieved tubing. The product is called BETACLAD™ and is discussed in more detail in the corrosion section of Chapter 6 on Properties. The process is modified when hollows of "barrier clad" are treated. In this case only the outer portion of the hollow is heated into the beta region while the inner surface is cooled and remains unaffected.

As a general rule, beta quenching the billet prior to extrusion removes the contribution of earlier metal working and heat treatments to the metallurgical structure. For this reason, little attention is currently paid to the effects of microsegregation in ingots or the thermal history used to forge and roll the bars used for the extrusion billets. Thermal treatments subsequent to the beta quench are very

important and determine the corrosion and mechanical properties of the tubing.

Mechanical Working

Some early processes included a hot working step after the beta quench to refine the grain size for extrusion or simply to reduce the bar to the size needed for the extrusion billet. This hot working is usually done with a preheat to between 500 and 780°C so that the structure remains in the alpha phase. This process has not been widely used in the last five years, but is of interest because of the effect that the heating for the hot working step may have had on intermetallic particle growth which is a key feature of interest in corrosion resistance. Nearly all of the tubing made in the 1970's and early 1980's was made with the alpha forging step after the beta quench.

The extrusion step is nominally a hot working operation conducted in the alpha phase region. In some cases, it is metallurgically a cold working operation in that the extrusion does not recrystallize during the working. Extrusion processes, both with and without concurrent recrystallization, are in common use. In those cases where the resulting structure consists of elongated grains typical of cold worked material, an anneal is used to recrystallize the extrusion before the first cold working step. Since the amount of residual cold work is relatively small, the anneal temperature is kept around 625°C to prevent a large grain size from developing. Thus far, both processes seem capable of producing tubing of equivalent performance.

Cold Pilgering

Manufacture of fuel clad tubing requires a series of cold working steps to reach the final size. Cold pilgering is used exclusively for cold reduction of

fuel cladding. The process starts with an extrusion which is over three inches (80 mm) in diameter. The deformation and metal flow during these cold working steps cause the metal crystals to align themselves in the tubing (preferred orientation or crystal texture). This phenomenon is covered later in this chapter with an appropriate introduction to the crystallography of the hexagonal close-packed structure.

Except for the crystallography, the metallurgy of the cold working is simply mechanical distortion of the structure followed by anneals to recrystallize the cold worked structure for the next step. The cold reductions are generally large, of the order of 60 to 80 percent reduction in area. These reductions are more than enough to assure a uniform fine grain size after anneals, generally ASTM 10 or finer. The reason cold pilgering is used rather than drawing lies in the economics of the process and the metallurgical requirements for control of crystal orientation. Cold drawing is limited to 15 or 20 percent reductions in area between anneals and must employ lubricants which are difficult to remove.

SANDVIK employs conventional cold pilger processes using a stationary tapered mandrel for all except the last reduction pass. The final cold reduction is made by a patented process on a moving cylindrical mandrel so that essentially all of the reduction is in the wall thickness. This produces a very stable and desirable radial orientation of the metal crystals.

Heat Treatment

Intermediate anneals are required between the cold pilger reductions to soften the metal for succeeding reductions. For many years, this softening was the only consideration in this step. In the 1980's, a relationship between the metallurgical

structure and corrosion resistance was found that added a new, and as yet incompletely understood, dimension to the role of the intermediate heat treatments. Here Zircaloy-2 and Zircaloy-4 differ as do the corrosion regimes that they usually face in power reactor service. Zircaloy-2 is the predominate cladding for BWR's and Zircaloy-4 is used in PWR's.

The following is a relatively simple treatment of a very complex technical area. There are many diverse speculative hypotheses as to the metallurgical mechanisms behind the observations. It has been found that rapid cooling of Zircaloy-2 from the beta phase, followed by cold working and annealing at the lowest possible temperatures and times, produce the best resistance to nodular type corrosion in the BWR. SANDVIK's research lead to a patented process employing a beta quenching operation near the end of the cold reduction process. Only one intermediate anneal was needed between pilgering of the quenched hollow and pilgering to the final tube size. The process can also be applied just prior to the last cold reduction, but the resulting structure contains some residual transformed beta platelets and lacks the desired uniformity for stress relieved cladding.

In contrast, it has been found that Zircaloy-4 requires a certain minimum time and temperature in the intermediate anneals to develop the best corrosion resistance in the PWR environment. There have been many attempts to correlate this behavior to the intermetallic compound size and distribution. They have produced interesting but incomplete explanations of the corrosion behavior. Determination of particle size and distribution in the sub-micron size range is difficult at best and there are many disagreements between investigators in the methods used and the

results obtained. Particle size is useful in research, but useless for specification purposes.

Since a number of intermediate anneals are used and each can vary in temperature and duration, an annealing parameter has been proposed to generate a number that can be used to correlate corrosion behavior with processing history. The equation most used is modeled after the tempering parameter used for steel heat treatment.

$$A = \sum t_i \exp (-Q/RT_i)$$

where A is the cumulative annealing parameter

t_i is the time in hours at temperature T

Q is an activation energy

R is the gas constant

T_i is the temperature in Kelvin

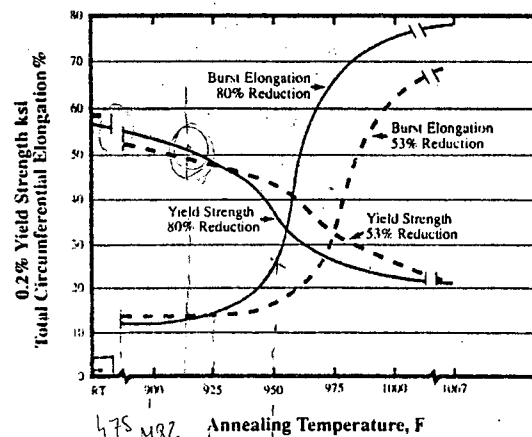
The most commonly used activation energy, 80,000 cal/mole, is based on the activation energy for recrystallization. Andersson, of SANDVIK, determined the value to be 63,000, based on actual measurements of corrosion tests made at 400C. In yet another study, Wadier of CEZUS developed a value of 37,400 using the Ostwald ripening theory for particle growth in zircaloy. Again, like the particle size, the annealing parameter is useful in developing an understanding of the various underlying mechanisms affecting corrosion, but it also is not the entire story. The very distinct difference in corrosion behavior shown in Figure 6-13, between stress relieved and recrystallized Zircaloy-4, is not predicted by the infinitesimal difference in the calculated cumulative annealing parameter. It is also difficult to assign an annealing parameter to a production lot where different parts of a furnace load have seen not only differences in the anneal temperature, but much different heating and cooling paths. There has been pressure to use annealing parameter in specifications, but as yet no consensus on its calculation technique has been established.

The final heat treatment of fuel cladding may either be a so-called "stress relief anneal" (SRA) or a full recrystallization anneal, depending on the particular application. In most instances, the stress relief anneal is really a partial recrystallization to reach a desired balance of strength and ductility.

↓ The range of strengths and ductilities that can be developed through variation in the amount of cold work and the final anneal temperature is illustrated in Figure 5-5. Cold reductions of 80% in the final cold pilger operation produce a relatively small increase in strength over smaller reductions of about 50%, but result in much improved ductility, particularly in the burst test. The strength curves for the two levels of cold work cross as the anneal temperature is increased because the higher level of cold work causes recrystallization to begin at lower anneal temperatures. The amount of cold work in the last reduction also affects the creep strength as will be discussed later. The curve is nearly flat, up to about 475°C, as only true stress relief is occurring. Beyond 475°C, recrystallization

Figure 5-5

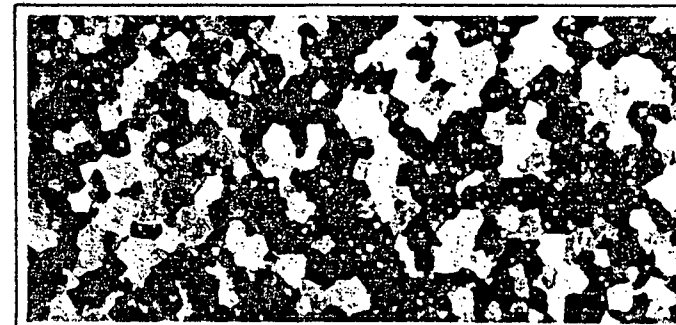
Effect of
Final Anneal
Temperature on
Cold Worked
Zircaloy Tubing



begins and the strength falls off rapidly with increasing anneal temperature until recrystallization is complete and no further reduction in strength occurs. The slope of the curve in the region of partial recrystallization depends on the amount of cold work in the final pass. The higher the cold work the steeper the rate of reduction in strength. Very accurate and uniform heat treating equipment that can hold temperatures to plus or minus one degree Celsius is needed to provide tubing with uniform properties when the desired strength level is in this region of rapid change. The strength and ductility of zircaloy do not change uniformly with the temperature at which the strength is determined. There is a leveling off of the strength and a sudden decrease in ductility in the region between 200 and 350°C as shown in Figure 6-2. The behavior is known as "strain hardening" and is caused by interstitial elements that diffuse through the structure and interfere with the movement of dislocations. At still higher test temperatures, the strength falls again and the ductility rapidly increases.

Figures 5-6 and 5-7 show typical microstructures for finished tubing in both the stress relieved and recrystallized conditions. The views are longitudinal to illustrate the elongated grains and the large amount of distortion in the stress relieved structure.

Figure 5-6



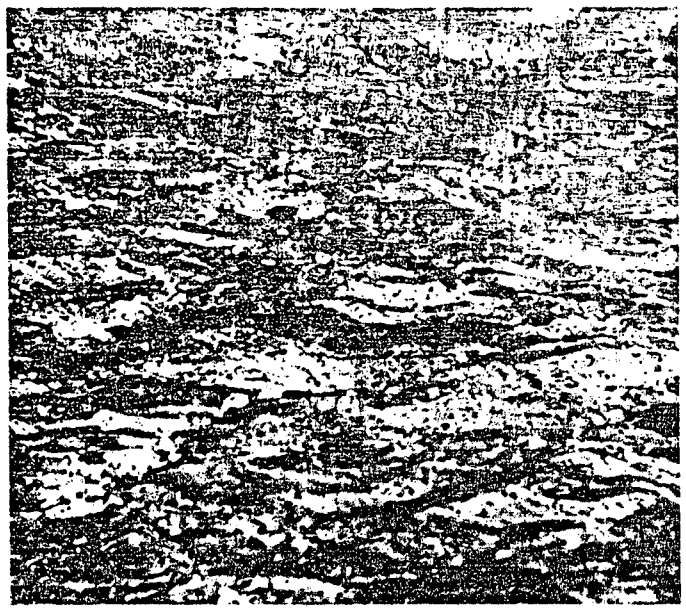
Micrograph of
Typical
Recrystallized
Tubing Showing
Equiaxed Grain
Structure and
Uniform
Distribution of
Intermetallic
Compound
Particles

Polarized
Light 700x

Figure 5-7

Micrograph
of Typical
Stress
Relieved Tubing
Showing
Distorted
Grains
Longitudinal
Section

Polarized
Light 700x



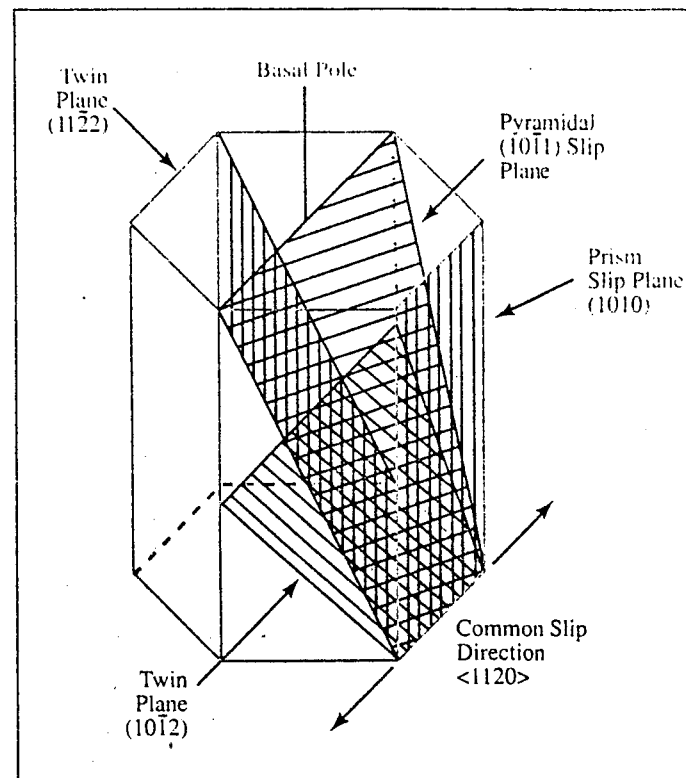
Crystallography

The hexagonal crystals that comprise zircaloy products play an important role in many of the properties of interest to fuel designers. To visualize the alignment of the crystals, the basal pole is used as a reference. The basal pole is a vector perpendicular to the basal plane of the crystal as shown in Figure 5-8.

Zircaloy deforms by both slip and twinning. Slip occurs only in the "a" direction on the prism and pyramidal planes as shown in Figure 5-8. Twinning occurs as a number of strict crystallographic relationships. The combination of twinning and slip leads to a strong preferred orientation of the crystals (texture) during cold working. While most of the deformation in cold pilgering is by slip, twinning is the process that rotates crystals of one orientation to another and thus is of the greatest significance to the metallurgist.

Figure 5-8

Orientation
of the
Important
Crystal Planes
in the
Hexagonal
Zirconium
Lattice



A random texture in a recrystallized tube as shown in Figure 5-9c would produce a tube with isotropic properties. The typical cold pilgered tube has a crystal texture with none of the basal poles oriented in the axial direction of the tube. The crystals are arrayed in the radial-circumferential plane perpendicular to the tube axis. A pure circumferential texture would be as shown in Figure 5-9b and a pure radial texture is shown in Figure 5-9d. It is not possible to produce pure textures in tubes and distributions of the basal poles in the radial-circumferential plane characterize various types of crystal textures.

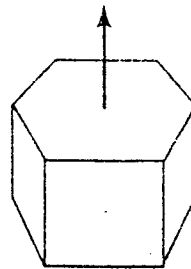
Cold pilgered tubing is characterized by having the greatest number of poles oriented at about

Figure 5-9

Illustration
of Crystal
Textures
in Tubing

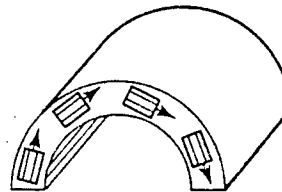
Basal Pole

- (a)
Unit Cell
Hexagonal
Close-Packed
Structure

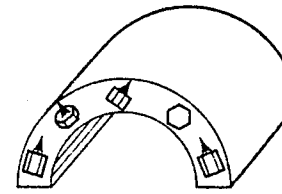


Cross-Section Through a Tube

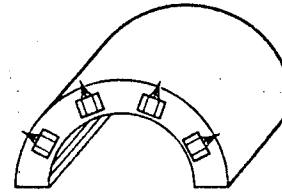
- (b)
Circumferential
Texture of Basal Poles



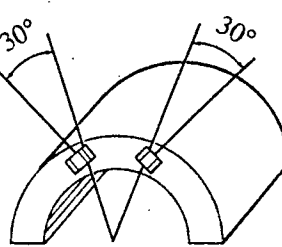
- (c)
Random Texture
of Basal Poles



- (d)
Radial Texture
of Basal Poles



- (e)
Usual Texture
of Basal Poles
in Tubing



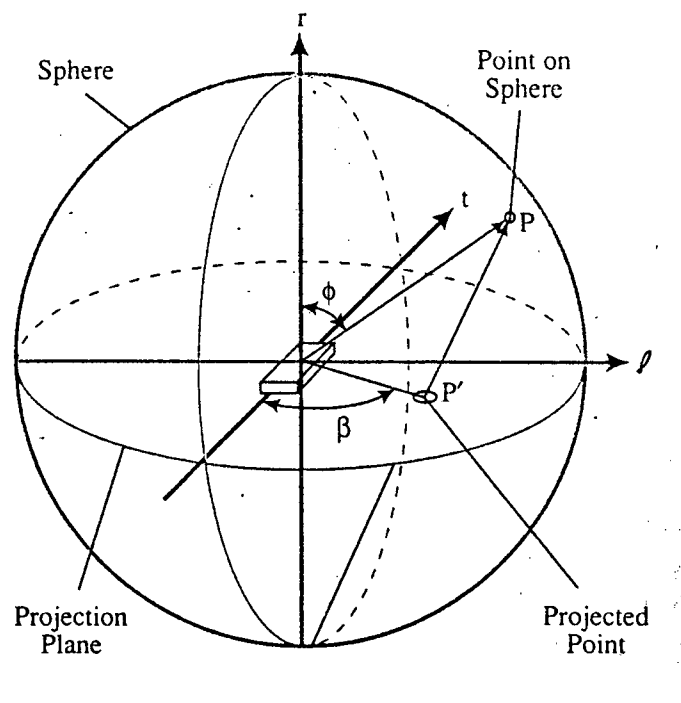
30 degrees from the tube radial direction. In the discussion of tube textures, those with most of the basal poles closer than 45 degrees to the tube radial are considered "radial" textures and those with most of the poles in the 45 to 90 degree region are called "circumferential." As will be seen in the later discussion, seemingly small differences in the orientations can have very significant effects on properties.

One of the most common methods for representing crystal orientation is the construction of a stereographic basal pole figure. Through the use of X-ray diffraction, the number of crystals in a sample oriented in each direction can be plotted. The basal poles are located by referring them to a three dimensional plot with the sample at the origin. The axes are: the axial direction (AD), the radial direction (RD), and the circumferential direction (CD). The circumferential direction is also known as the tangential direction. The intersection of each basal pole with a hemisphere sitting on the axial-circumferential plane is a point representing that crystal. Each of these points is projected back to the axial-circumferential plane as shown in Figure 5-10. A two dimensional plot of the density of the points which represent the crystals is obtained. Lines are drawn outlining regions of equal density of the crystal orientations much like a contour map. The contour lines represent multiples of random orientation.

The pole figure is made from a sample of the tube that has been thinned by acid etching and then elastically flattened and attached to a specimen holder for examination in the x-ray goniometer. The technique can measure the texture at different points through the tube wall, depending on how the sample is thinned. A relatively simple reflection technique can measure the intensity of the planes that are closer than 70 degrees to the radial

Figure 5-10

Principle of the
Stereographic
Projection Used
to Prepare
Pole Figures



direction, but a more complex combination of reflection and transmission is needed to determine the entire pole figure. A very detailed explanation of the procedure for making pole figures was published in a paper by Wilson, of SANDVIK, in the Scandinavian Journal of Metallurgy.

Stereographic pole figures can be constructed for any crystallographic plane. A pole figure made from the prism planes shows that recrystallization has a marked effect on the prism plane orientation even though it has only a very small effect on basal plane orientations. Most of the properties of interest are related to the basal plane orientations and this pole figure is seen most often.

The stereo pole figure presents all of the information about crystal orientations, but is difficult to

interpret. Since all of the basal poles lie near the radial-circumferential plane, a section through the pole figure on this plane will present the most important data, which is the relative density of crystals oriented in that plane. It is easier to see the significant features of the basal pole distributions, as shown in the basal pole figures and their corresponding cross section plots, in Figure 5-11. The heights and widths of the basal pole distributions are the key features in interpreting the effect of texture on properties.

Neither the basal pole figure nor the cross section plot provide a numerical index of texture for use in statistical correlations with other properties. Several such indexes have been proposed. One is simply the angle from radial (ϕ) at which the density of basal poles is the greatest; the peaks in the plots shown in Figure 5-11. A second widely used set of index numbers are the Kearns parameters, which give the effective fraction of basal poles in each of the directions. These are simply geometric resolutions of vectors of basal poles and are expressed as relative to random occurrence. The Kearns parameters sum to one. The most frequently used number is the representation in the radial direction, f_r . The value of f_r for each of the textures is given in Figure 5-11.

The contractile strain ratio, or CSR, is a simple measure of crystal texture. It requires only a tensile test machine and some very accurate measuring devices rather than the complex x-ray equipment needed to construct a pole figure. The test procedure is described in Chapter 4 and produces a number related to texture. The ratio of the Kearns parameters f_r/f_t is approximately equal to the CSR value, as shown in Figure 5-12. Values for CSR of one or less represent circumferential textures, while values of two or greater are strongly radial.

Figure 5-11

Methods of
Representing
Crystal Textures,
Pole Figure,
Intensity Plot,
Kearns
Parameter,
and CSR Value

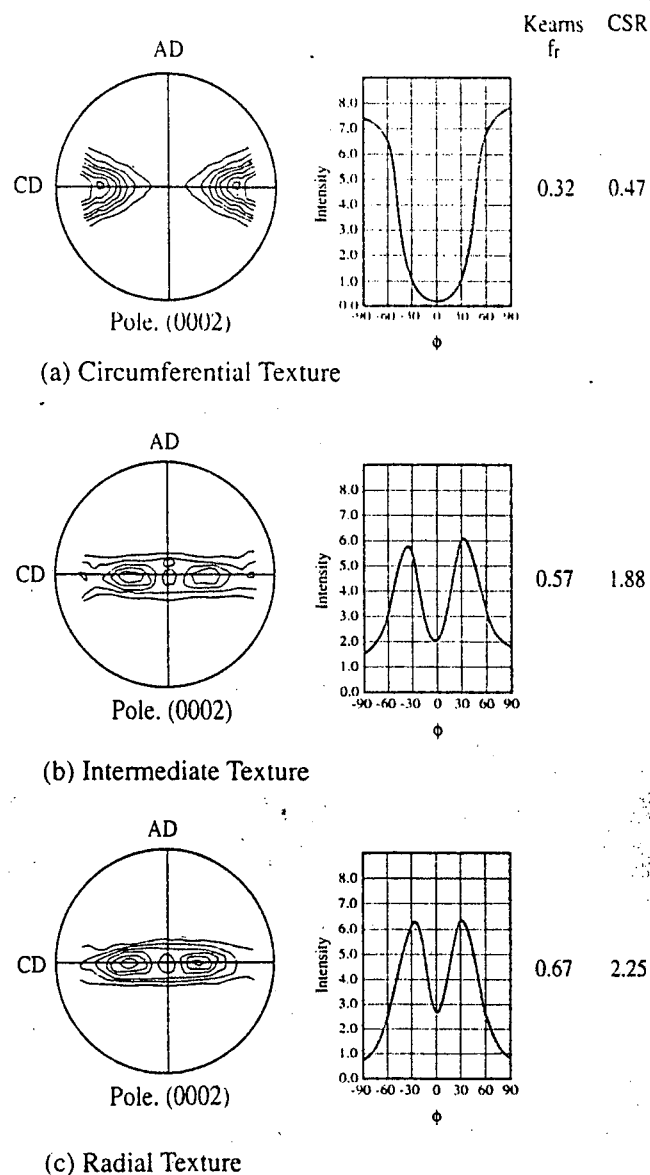
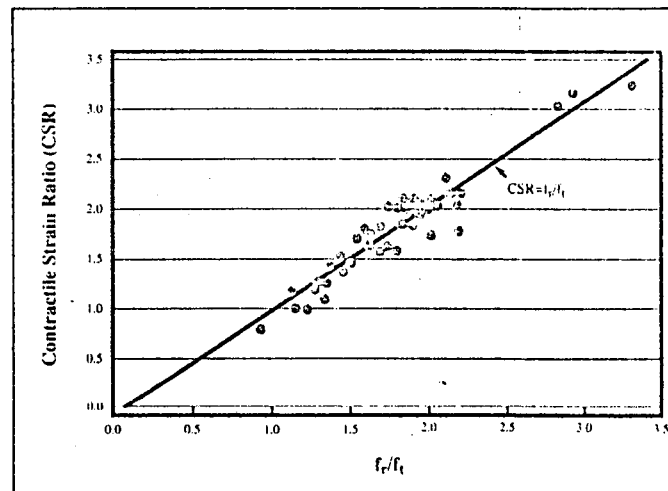


Figure 5-12

Relationships
of Contractile
Strain Ratio to the Ratio
of Kearns
Parameters



Since slip provides the path of least resistance to deformation and it occurs only in one crystal direction, a tube will have very different mechanical properties depending on the texture. In a longitudinal tensile test, both radial and circumferential textures have the primary slip direction oriented parallel to the stress and exhibit the same strength, though the deformation is much different. A radial texture resists wall thinning and promotes diameter change and so the tube necks down during straining, which is similar to tensile tests on ductile materials. A circumferential texture resists diameter change and favors wall thinning and the deformed tube remains at a nearly constant diameter right up to fracture.

The control of crystal texture enables a fuel designer to choose, within some limits, the directions of greatest strength and maximum ductility. To take advantage of this relationship, it is essential that the texture be uniform and controlled if the properties of the tubing are to be the same from tube to tube and lot to lot. Tenckhoff, in ASTM STP 966, provides an excellent detailed description of texture, deformation, and anisotropy in zircaloy.

Properties such as hydride orientation, irradiation growth, creep, iodine stress corrosion cracking resistance, and even resistance to corrosion in water and steam are affected by the orientation of the metal crystals, as will be discussed in Chapter 6 on Properties and Performance.

Figure 5-13

Basal Pole Figure and Intensity Plot for Typical SANDVIK Cladding

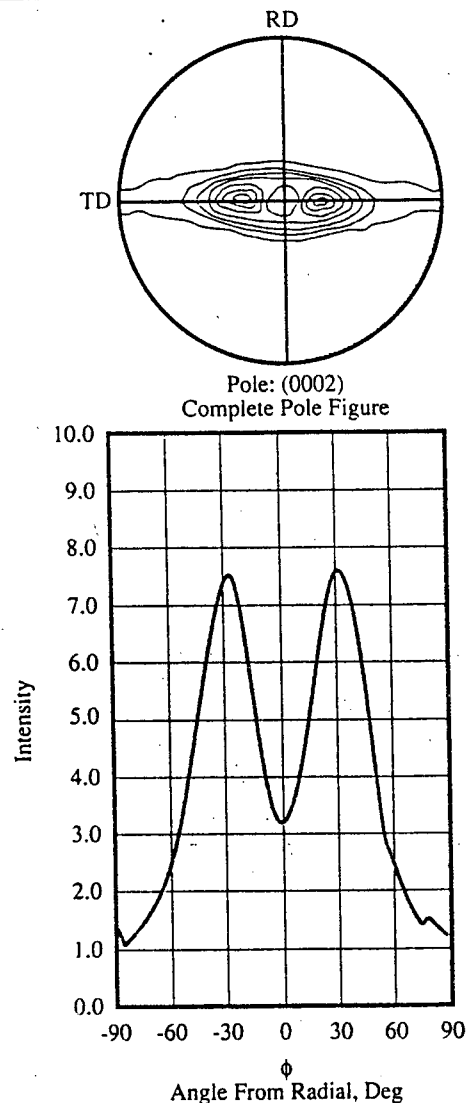
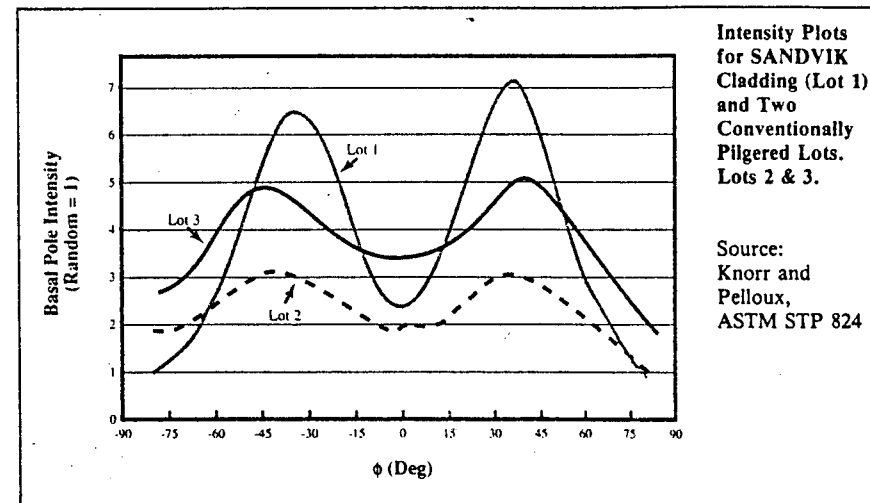


Figure 5-13 represents a typical sample of SANDVIK's current fuel clad tubing. The basal plane orientations of the crystals are determined by the reductions employed in its manufacture. Heat treatment strongly affects the prism texture, but has a lesser impact on the basal texture. The unique reduction technique used by SANDVIK results in a relatively narrow band of distribution, closer to radial than those produced by the conventional process. Figure 5-14 illustrates this difference.

Figure 5-14



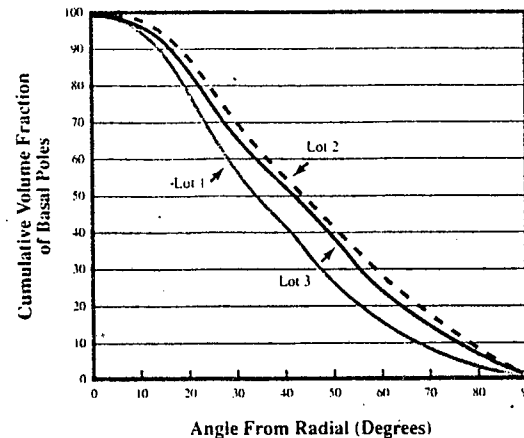
Source:
Knorr and
Pelloux,
ASTM STP 824

ference. Lot 1 is SANDVIK tubing and is characterized by the narrow high peaks at about 30 degrees from radial. Lots 2 and 3 were produced by different versions of conventional processing and have more random textures with low flat peaks, which are somewhat further from the radial direction. Another way of presenting the distribution of orientations is shown in Figure 5-15. Here we see the cumulative volume fraction of the crystals oriented at various angles from the radial direction. The same three lots are represented in both Figures 5-14 and 5-15. This particular presentation is useful in understanding the resistance of zircaloy

Figure 5-15

Comparison of the Cumulative Volume Fraction of Crystals Oriented in the Regions Measured from the Radial Direction for the Lots Shown in Figure 5-14.

Source:
Knorr and
Pelloux,
ASTM STP 824



tubing to iodine stress corrosion cracking, which will be taken up later in Chapter 6 on Properties and Performance.

The development of the crystal texture in tubing is often characterized by a ratio of wall reduction to diameter reduction called, the "Q" ratio. Q was first defined simply as the ratio of percent reduction in wall thickness divided by percent reduction in outside diameter. Later, it became relatively standard to use the mean diameter of the tube to calculate the ratio. A ratio of the natural strains (QE) results in slightly different values. QE is more useful because a series of reductions of the same QE ratio results in the same ratio overall where Q does not.

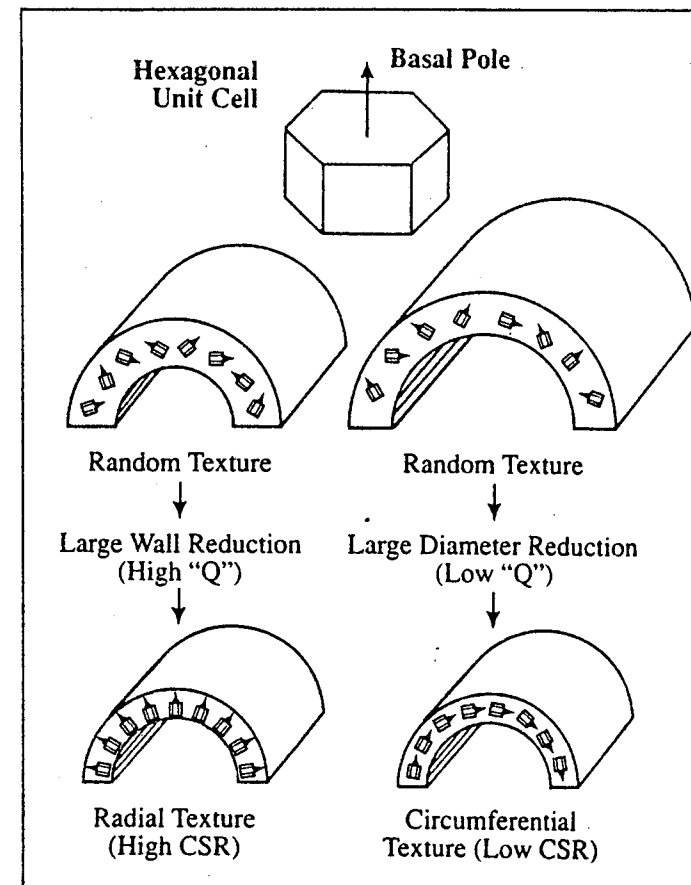
$$QE = \ln(W_1/W_2) / \ln(MD_1/MD_2)$$

where W_1 is the initial wall thickness
 W_2 is the final wall thickness
 MD_1 is the initial mean diameter
 MD_2 is the final mean diameter
 $\ln$ is the natural logarithm

Reduction steps can then be characterized by the reduction in area and the Q or QE ratio. This characterization, illustrated in idealized form in Figure 5-16, is quite useful. Like the others in this book, they tell only part of the story. The pure textures in the figure cannot be obtained by pilgering. High Q values for a reduction pass tend to rotate the crystals so that their basal poles are closer to the radial direction. Reductions with Q values less than one tend to produce crystal orientations close to the circumferential texture. It is possible to come closer to the ideal circumferential texture than the radial one. The Q ratio can vary

Figure 5-16

Illustration of the Effect of "Q" Ratio on Texture Development During Pilgering



along the reduction cone of each pilger pass and cause the texture, resulting from two different sets of tooling, to be quite different even though the Q ratios are the same. This relationship was explored by Schemel and McKenzie in ASTM STP 551.

This chapter has explored the various metallurgical features that each step of the process presents. It is important to recognize the relationships for what they presently are. They are very useful tools in developing an understanding of the metallurgical phenomena that take place as zircaloy tubing is manufactured, but as yet they are only guides and not precise predictors of properties or performance.

Chapter 6

Properties and Performance

This chapter presents the physical, mechanical, and corrosion properties of interest to the fuel design engineer. They are taken from a variety of sources both new and old. Where the value is crucial to the application in question, it is suggested that the value be taken directly from an original document so that the method of determination and reliability can be assessed.

Zirconium

Atomic Number 40

Atomic Weight 91.22

Lattice Parameters

HCP $a = 3.2312$ angstroms

$c = 5.1477$ angstroms

BCC $a = 3.6090$ angstroms

Natural Isotopic Composition

Mass No.	Percent
90	51.46
91	11.23
92	17.11
94	17.40
96	2.80

Zircaloy -2 or -4

Density

0.237 lbs/cu. in.

6.55 g/cc

Electrical Resistivity

74 micro-ohms/cm

Thermal Conductivity
(300C)

0.037 cal/cm sec deg C

Table 6-1

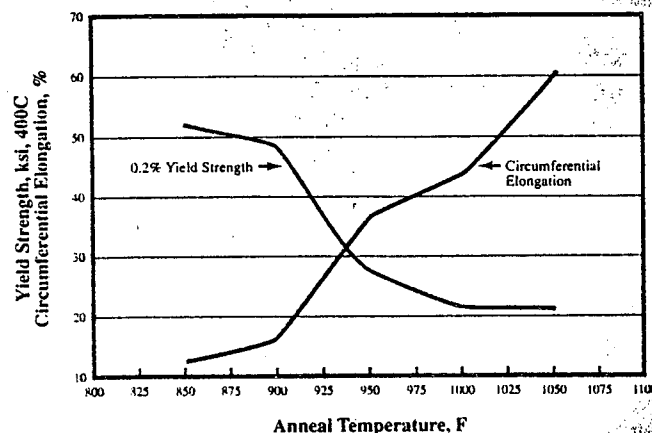
THERMAL NEUTRON CROSS SECTIONS	
	Barns
Beryllium	0.009
Magnesium	0.059
Lead	0.17
Zirconium	0.18
Zircaloy -4	0.22
Aluminum	0.23
Tin	0.63
Niobium	1.1
Nitrogen	1.9
Iron	2.56
Molybdenum	2.55
Austenitic stainless steel	3.1
Nickel	4.5
Titanium	6.1
Hafnium	104
Boron	750
Cadmium	2,520
Gadolinium	48,890

Mechanical Properties

The mechanical properties that can be attained by variation of the amount of cold work and the annealing temperature were explored in Chapter 5. Figure 6-1 illustrates the strength and ductility

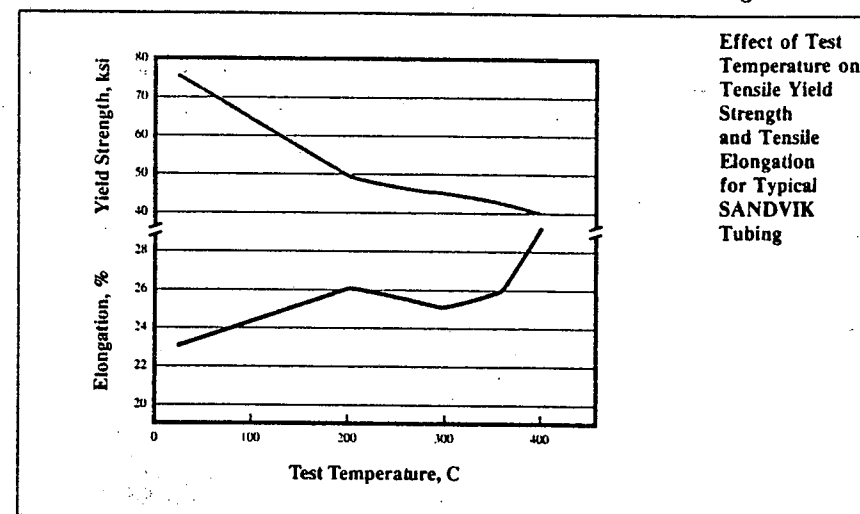
Figure 6-1

Effect of Final Anneal on Tensile Yield Strength and Circumferential Elongation in a Room Temperature Burst Test for Typical SANDVIK Tubing



relationships over a variety of anneal temperatures for SANDVIK cladding when tested at 400C. Relationships at other test temperatures are similar. The flat upper portion of the strength curve represents the true stress relief section, the steeply descending section is partly recrystallized, and the lower flat portion represents fully recrystallized tubing. Zirconium and zircaloy exhibit an unusual relationship between test temperature, strength, and ductility. The effect is called strain aging and is illustrated in Figure 6-2.

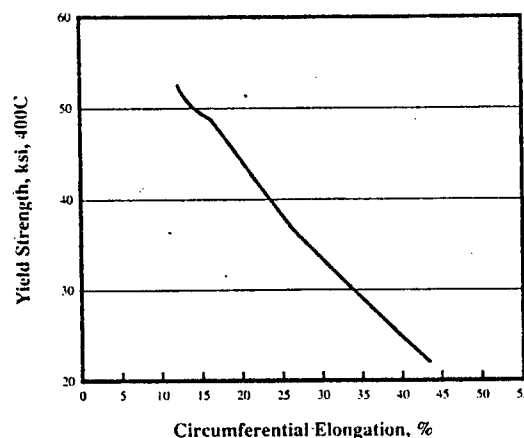
Figure 6-2



Note the plateau in strength and elongation in the 200 to 350C range. The strength levels off while the elongation decreases with increasing temperature for a period. The balance between strength and ductility are best shown by the comparison of yield strength and circumferential elongation in a burst test over a range of strengths as shown in Figure 6-3. In general, the SANDVIK cladding will exhibit more ductility at each level of strength than tubing made by the conventional processes.

Figure 6-3

Relationships of
Tensile Yield
Strength and
Circumferential
Elongation in a
Burst Test
for Typical
SANDVIK
Tubing



Corrosion

Zirconium and, to a lesser extent, the zircalloys are resistant to a wide range of inorganic and organic acids and bases with the exception of hydrofluoric acid, which attacks them quickly. A very complete treatment of chemical corrosion resistance can be found in Volume 13 of the Metals Handbook, Ninth Edition. In that article, zircaloy is called grade 704 and Zirconium-2.5Nb alloy is called 705.

It is resistance to water and steam at reactor temperatures that is of the greatest interest to the fuel designer. This section is developed historically for clarity and recognizes that the field is not yet completely understood. New work will certainly modify even the best hypotheses held at the time this is written.

The alloys of zirconium depend on the formation of a tightly adherent and protective oxide film for their resistance to corrosion. Corrosion in the nuclear reactors can be measured only at the intervals between refuelings, which provide only a few data points on the curve of oxidation rate.

Therefore, corrosion is studied primarily through tests in autoclaves where water or steam can be used to simulate reactor corrosion. Most investigators use a temperature higher than that experienced in the power reactors to accelerate the corrosion so that tests can be completed in a shorter time. There is some danger in such accelerated tests, since the mechanism of corrosion may change rather than simply be accelerated by the increase in temperature. This is particularly true in the 400 to 500°C range where the mechanism changes from uniform corrosion to nodular type corrosion. In some cases, in or out of reactor loops are used to better simulate the actual service conditions, particularly the effects of thermal flux, irradiation, and water chemistry.

Contrary to the early studies, Zircaloy-2 and -4 are quite different in their metallurgical makeup and performance in power reactors. The better resistance to steam in an oxidizing media makes Zircaloy-2 the choice for cladding in BWR's while the lower hydrogen pickup fraction makes Zircaloy-4 the current choice in PWR's, which run with an over pressure of hydrogen.

Both alloys form a sub-stoichiometric oxide film when exposed to water or steam. This film retards the flow of oxygen to the metal-oxide interface and the corrosion slows down as the film builds up. Investigators have characterized this relationship as quasi-cubic in nature. After a period of time, the oxide film loses its protective nature and the rate increases again. Early investigators characterized this behavior as a transition from the cubic to linear reaction kinetics. In 400°C steam, the transition occurs after about 40 days and at a weight gain of about 40 mg/dm². Since the initial weight gain was small, the post transition rate of weight gain was used as the best index of performance. Figure 6-4 is taken from an early

Figure 6-4

Corrosion Data
for Zircaloy-2
and Zircaloy-4
in Steam
and Water

Source: Kass,
ASTM STP 368

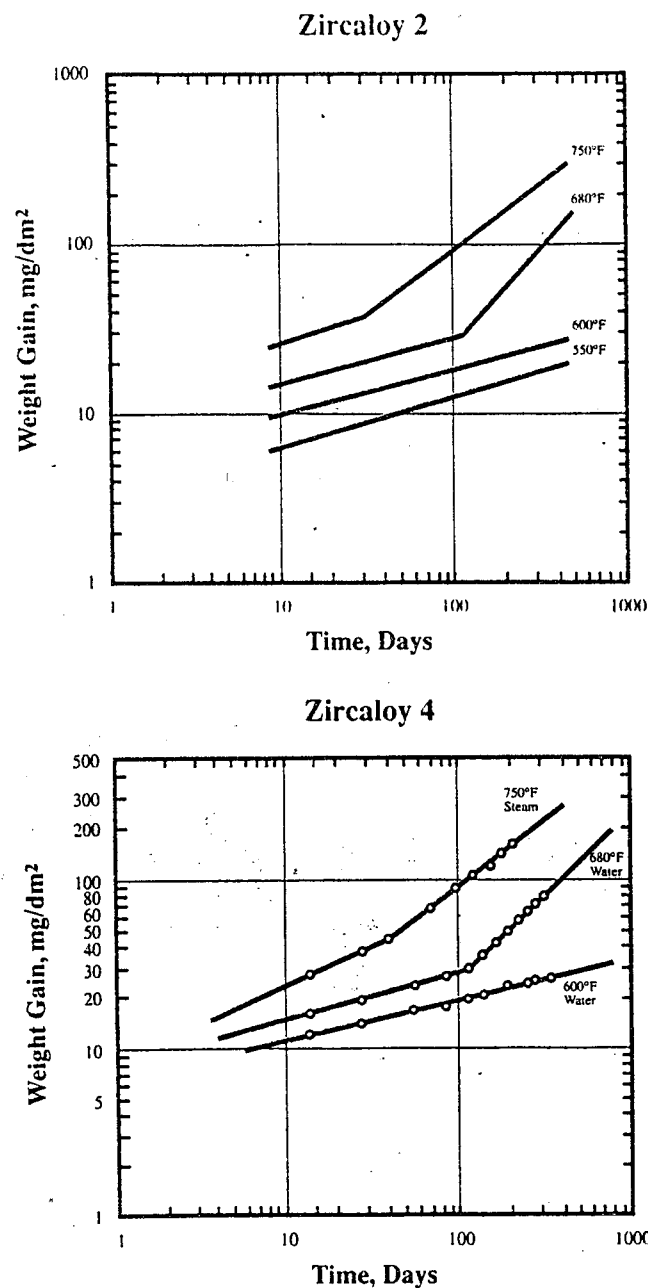
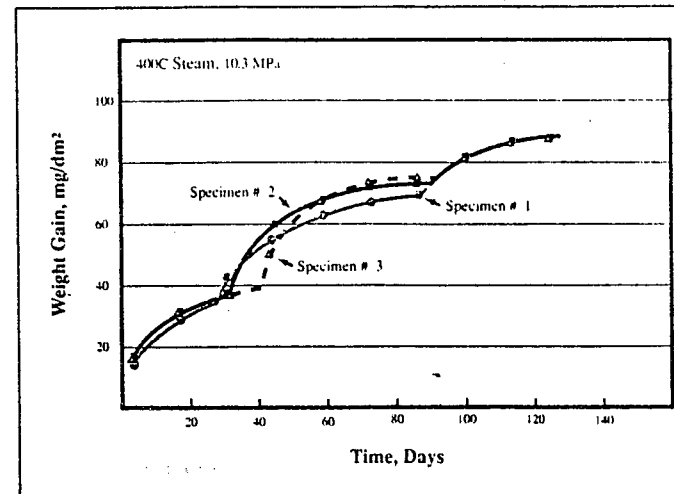


Figure 6-5

Illustration to
the Repeating
Quasi-cubic
Weight Gain
Cycles for
Corrosion of
Zircaloy-4 in
400C Steam

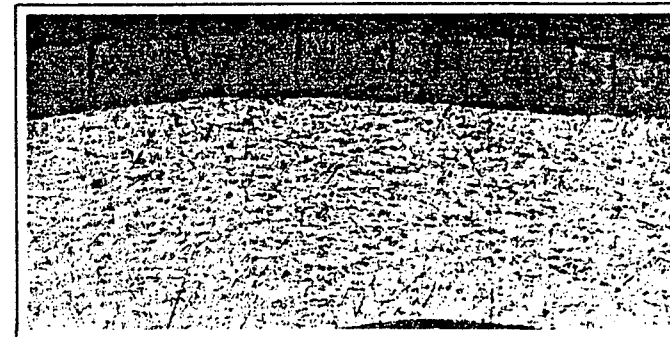
Source:
Schemel et al,
ASTM STP 1023



paper of Kass in ASTM STP 368 and illustrates the concept.

Later on more precise work has shown that the corrosion kinetics do not change to linear behavior, but the film goes through a succession of quasi-cubic behaviors. This suggests that the film breaks down to allow oxygen to more freely reach the metal oxide interface, but then the protective film begins to form again and the rate again declines as shown in Figure 6-5. The resultant oxide is shown in the cross section of a thick oxide film in Figure 6-6. More recently Peters

Figure 6-6



Micrographic
Section Through
a Thick
Oxide Film on
Zircaloy

Bright
Field 100x

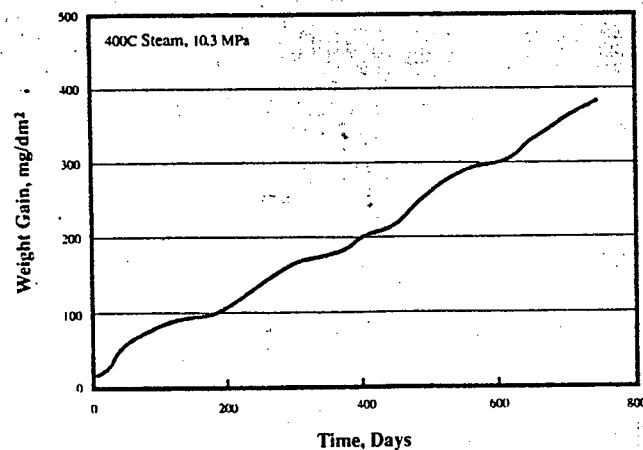
reported in STP 939 that at very long times in 360C water tests, the quasi-linear post transition oxidation rate nearly doubled after about 1000 days of testing.

SANDVIK has been using the 400C steam corrosion test to study behavior of various samples of fuel cladding. After exposure for over 60 days in this test, some specimens departed from the cyclic rate transitions to very high and ever increasing oxidation rates. The time to this type of transition seems to be related to in-reactor corrosion behavior as proposed by Schemel et al. in STP 1023. Most of the normal cladding materials in this test continue to show the cyclic behavior, even after 700 day's exposure and weight gains of 400 mg/dm² or approximately 27 microns of oxide film thickness. A representative weight gain curve is shown in Figure 6-7. The uniform corrosion described up to this point is typical of behavior in PWR's and autoclave tests up to about 425C.

In the 1970's, a different type of corrosion was noticed in BWR's. This corrosion produced small nodules of white oxide in the film of the uniform

Figure 6-7

Typical
Corrosion
Weight Gain
for SANDVIK
Zircaloy-4
Tubing Tested
in 400C Steam

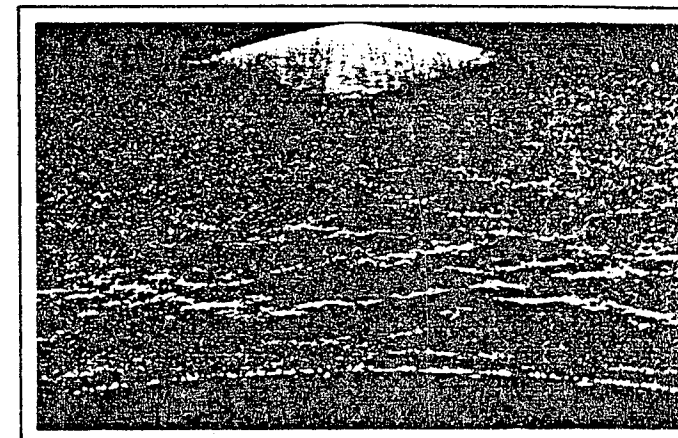


black oxide. This type of corrosion had been noticed earlier in autoclave tests by Johnson at the Hanford Laboratories and reported in STP 458. An example of nodular corrosion is shown in Figure 6-8, which includes a cross section showing the nodule and the surrounding uniform black oxide film.

In some BWR's, this type of corrosion was made more severe by the presence of a hard CRUD layer containing copper and resulted in some fuel failures. There is no consensus on the mechanism of formation of the nodules or the microstructural feature that may nucleate them. One-day autoclave tests at 500 to 520C in steam are used to simulate the phenomenon for study.

The relationship between autoclave test results and in-reactor corrosion rates have been postulated by many investigators, but without a real consensus developing. Most assign an "enhancement factor," determined by comparing the autoclave result with measured oxide film thickness on irradiated fuel rods from the same tube lot. The details of the corrosion models used to predict oxide film thickness on fuel rods in reactor service is beyond the scope of this book.

Figure 6-8



Micrographic
Cross Section
Through a
Corrosion
Nodule
Developed in a
500C Steam
Corrosion Test

Dark Field 70x

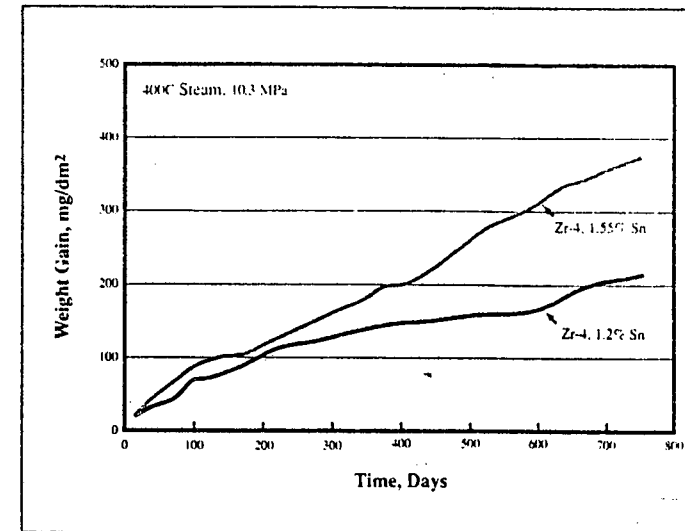
The discussion of composition, heat treatment, and other factors will be based on autoclave test data with reference to confirming in-reactor data where it is available.

Composition Effects

Composition of the zircaloys was established by the Naval Nuclear Propulsion Program and has remained relatively unchanged for 30 years. Some elements were originally classified as impurities, but are now known to be essential or desirable alloying elements. Oxygen, silicon, and carbon are former impurities that are now considered beneficial alloys. The two elements, with strong adverse effects on corrosion resistance; are aluminum and nitrogen.

The alloy contents of the zircaloys are compromises between corrosion resistance, strength, and workability. Kraftwerke Union of Germany presented work showing that samples of Zircaloy-4 with a tin content near the lower limit of the usually specified range (1.2 to 1.7%) had better corrosion resistance than samples with tin contents near the high end of the range. The effect is illustrated in Figure 6-9, which compares the weight gain of an alloy containing 1.2% tin to one containing 1.55%. Both are stress relieved Zircaloy-4 cladding tubes tested in 400°C steam. In a similar type of study, Teledyne Wah Chang Albany (TWCA) showed that Zircaloy-2 with iron near the upper limit of the specified range (0.7 to 0.20%) had better resistance to nodular corrosion than those samples that had lower iron contents. In each case, the thermomechanical processing history of the samples strongly affected the corrosion result. It is not possible to consider composition independently of the processing. The thermal processes that bring out the best properties for one alloy in one type of test may not be optimum for another alloy or type of test. This applies to reac-

Figure 6-9



tor service, as well since BWR's and PWR's are quite different.

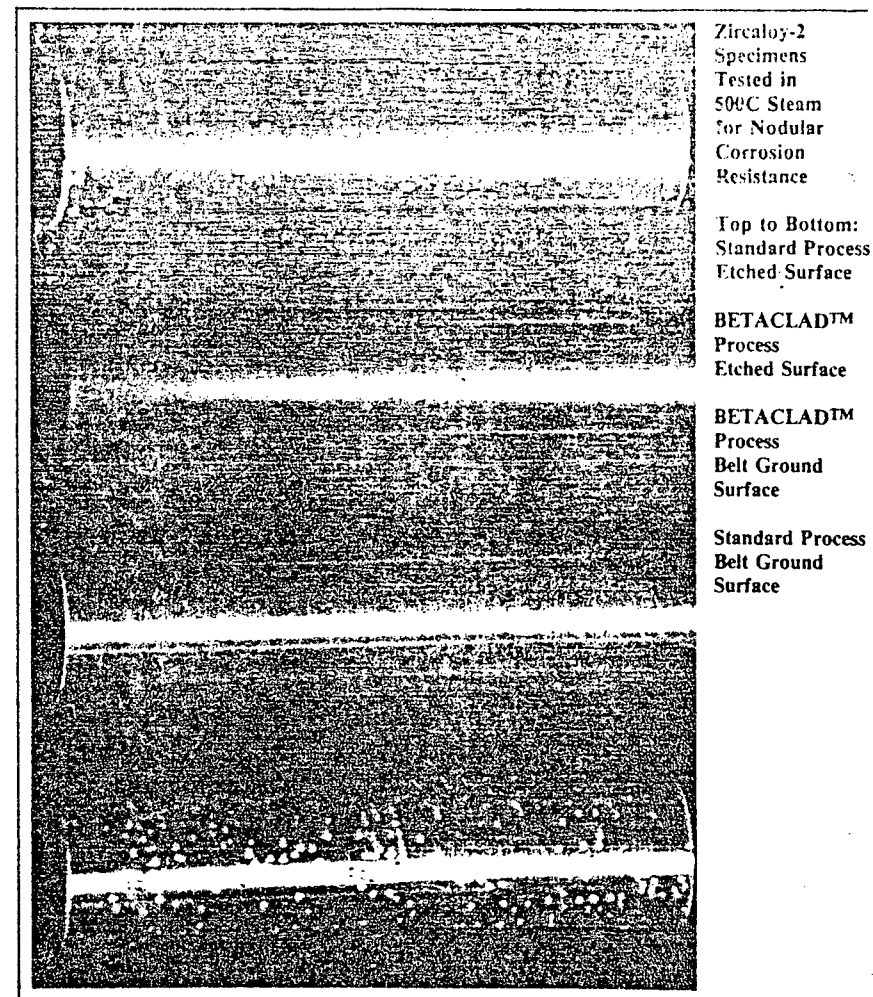
The composition limits in the specifications do not imply that unacceptable performance will result if the limits are exceeded. The values were set at a time when little was known of their significance and represent the best the industry could do at that time to make the materials uniform in composition. The evidence is clear that compositions outside the current limits for zircaloy will produce better corrosion resistance. It should be anticipated that these modified compositions will, after testing for not only corrosion, but also for needed strength and other properties, lead to a new series of alloys superior to the current zircaloys. Work is now underway to breathe new life into an old zirconium-niobium-tin alloy system studied earlier by the Russians.

Thermomechanical Processing Effects

The importance of the thermomechanical process in developing good corrosion resistance has been known since the 1960's when "beta quenching" was first introduced commercially. "Beta quenching" is a term used to denote a process where the zircaloy is heated above 1000C to an all-beta phase structure in which most elements are soluble, and then rapidly cooled, usually by a water quench. The beta quench structure gives good corrosion resistance, but poor ductility so that a practice of beta quenching the zircaloy part way through the metal working steps was adopted. The good dispersion of the intermetallic compounds could be retained while subsequent working regained the desired blend of mechanical properties. In the manufacture of tubing, beta quenching was done during the forging of the bars from which the extrusion billets would be cut. This relatively simple concept produced zircaloy fuel cladding with satisfactory corrosion resistance until the nodular corrosion phenomenon appeared in the BWR's and high-heat-duty fuel designs were used in PWR's.

Several techniques have been developed that reduce the incidence of nodular corrosion to some extent. SANDVIK's research produced a more dramatic result by introducing a "beta quench" step near the end of the cold reduction process. The tubing made by this patented process is called BETACLAD™ and is totally resistant to nodular corrosion, while retaining other desirable properties of SANDVIK's fuel cladding. Figure 6-10 shows specimens of standard and BETACLAD™ tubing with both a belt ground and an etched surface after being tested for 24 hours in 500C steam. Weight gains of BETACLAD™ in the 400C steam test are slightly higher than for standard cladding, but this has not

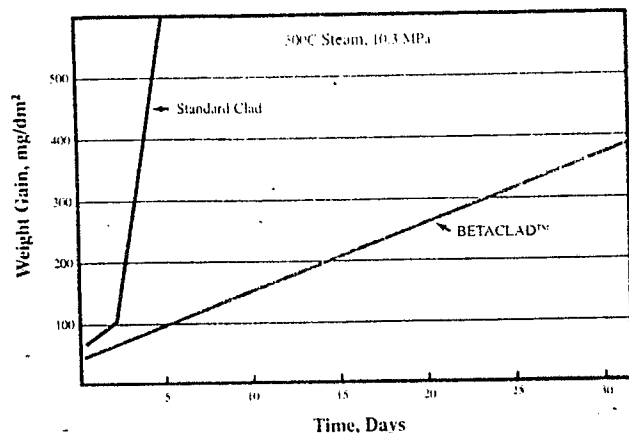
Figure 6-10



translated into unacceptable oxide film thicknesses in reactors. Figure 6-11 shows the difference between standard and BETACLAD™ tubing in an extended test in 500C steam. The BETACLAD™ continues a linear corrosion rate after 30 days, while the standard cladding disintegrated after about 5 days. Both, however, met the usual requirement in a 24-hour test.

Figure 6-11

Comparison of
Standard
Process
Zircaloy-2
Cladding and
BETACLAD™
in an
Extended Test
at 500C
in Steam



Many BWR's are running very satisfactorily with cladding made without the last beta quench step, but with the reduced intermediate anneal temperature. When reactor service conditions are severe, the BETACLAD™ provides the needed extra measure of protection.

Process modifications to the beta quench step have produced a distribution of very fine intermetallic phase particles. This has lead to better resistance to nodular corrosion in Zircaloy-2; but, the converse has been found for Zircaloy-4 in PWR's. Very fine precipitate particles have been found to lead to early departure from the cyclic corrosion behavior and thicker oxide films on fuel rods exposed in the hotter reactors. It is now generally accepted that some minimum amount of thermal energy, which results in the coarsening of the intermetallic particles after the beta quench, is necessary for good corrosion resistance in Zircaloy-4 cladding. This minimum thermal input is now expressed as a cumulative annealing parameter which was explained in detail in

Chapter 5 on Metallurgy. There is also evidence that the addition of silicon to about 80 ppm reduces the amount of thermal input necessary to achieve good corrosion resistance.

The relationship between the annealing parameter and corrosion for Zircaloy-2 and Zircaloy-4 is shown in Figure 6-12. For Zircaloy-2, the plot represents testing in 500C steam for nodular type corrosion while for Zircaloy-4 the plot is for testing in 400C steam for uniform corrosion. There is, as yet, no consensus on how the annealing parameter should be calculated and, given the variation in various parts of commercial heat treating furnaces, it is more properly shown as a band or range than a single value. It is possible to calculate maximum or minimum values of the annealing parameter for production materials, but not a single value for simple correlation purposes.

As shown in Figure 6-13, the effect of the final heat treatment on the corrosion of Zircaloy-4 tubing in 400C steam is quite marked, even though

Figure 6-12

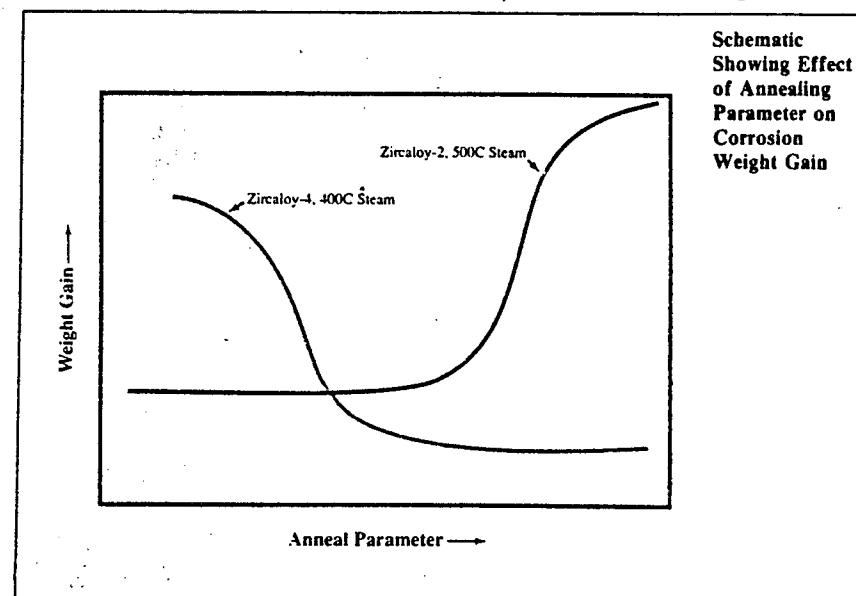
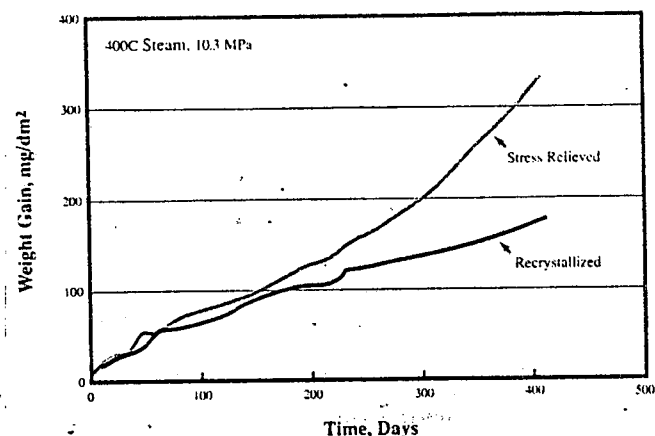


Figure 6-13

Comparison of Stress Relieved and Recrystallized Zircaloy-4 Tubing Tested in 400C Steam



the difference in cumulative annealing parameter is negligible. Recrystallized tubing has consistently lower weight gains than does the stress relieved cladding.

CEZUS, the French zirconium manufacturer, has shown that nodular type corrosion occurs more easily on some crystal faces than on others, so that crystal texture may play an important role in this type of corrosion behavior.

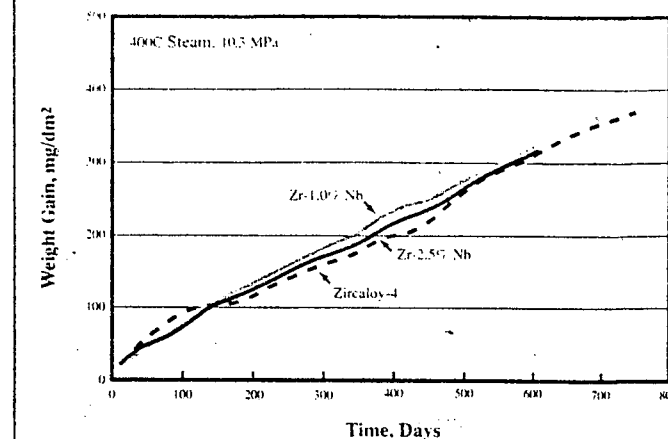
In Figure 6-14, corrosion resistance in 400C steam is shown for some other alloys used in nuclear service. The Zirconium-1Nb alloy is used in the USSR and the Zirconium-2.5Nb alloy is used in the CANadian Deuterium Uranium (CANDU) pressure tubes as well as for cladding in the Canadian organic-cooled test reactor.

Surface Finish Effects

For many years, the fuel clad tubes were made with a carefully etched outer surface which was oxidized in an autoclave prior to installation in a power reactor as a proof test of corrosion resistance. The BWR's continue, in some cases, to

Figure 6-14

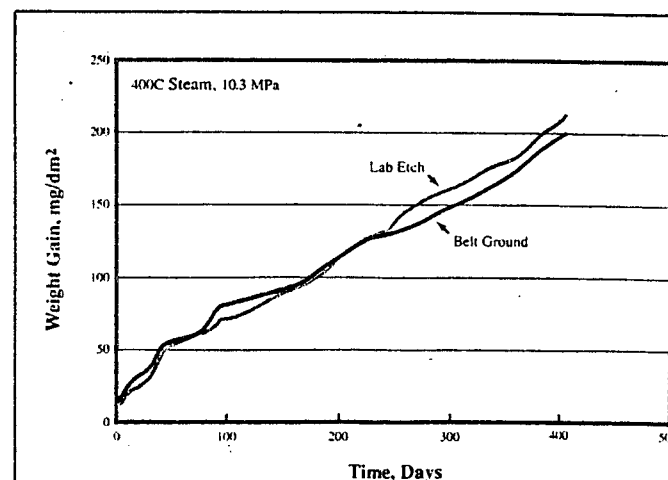
Comparison of Two Niobium Containing Alloys to Zircaloy-4 When Tested in 400C Steam



to use this preoxidation technique, but all PWR fuel rods and many BWR rods as well, are being installed with a belt ground outer surface and without preoxidation. As can be seen in Figure 6-15, the corrosion rate of etched samples is little different from belt ground ones in a long term test in 400C steam. Some investigators believe that preoxidation in

Figure 6-15

Comparison of Belt Ground Tube Specimens With and Without the Laboratory Etch



steam increases the oxidation rate in-reactor by forming a different type of oxide layer than forms in high temperature water.

Crystallographic Texture

The anisotropy of mechanical properties in tubing is only partly due to the elongated grains of cold worked and stress relieved microstructure. The zircaloy tubing, even in the annealed condition, exhibits a strong preferred orientation of the hexagonal crystals in the tubing. This preferred alignment of crystals is called crystallographic texture and was explained at length in Chapter 5 on Metallurgy. Texture plays an important role in yield strength, burst ductility, hydride orientation, iodine stress corrosion cracking, and even some physical properties like thermal expansion.

Creep

Creepdown of cladding during service is a major consideration in fuel design and performance. Stress relaxation, which is a manifestation of creep, is thought to play a role in pellet clad interaction (PCI). When time to hard contact with the fuel pellet is considered, a low creep rate is desired. When relaxation of stress at the pellet-clad interaction point is considered, a high creep rate that quickly reduces the stress level below that need for cracking is desired.

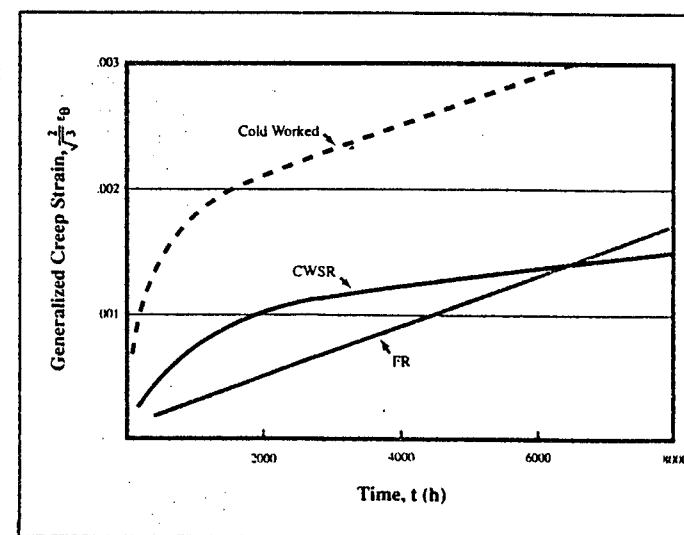
Creep or stress relaxation in zircaloy is not well understood. Franklin, Lucas, and Bement prepared a comprehensive book on *Creep of Zirconium Alloys in Nuclear Reactors*, ASTM STP 815. This section presents a simplified treatment of a very complex subject.

Although creep of the fuel rod results from external pressure, the phenomenon is usually studied by measuring the increase in diameter of

specimens pressurized internally and held at a constant temperature. Figure 6-16, taken from STP 815, shows the generalized creep behavior for zircaloy tubing. This work by Stehle of Kraftwerke Union (KWU) illustrates the problem in using short-term tests to predict long-term behavior. At one time, a test setting forth a maximum increase in diameter of 1 percent after 240 hours at 400C and 20,000psi was used. In this test, the highest values are found for cold worked tubing, just as shown for 320C in Figure 6-16. The diameter increase in the test decreased as the temperature of the final heat treatment was increased. The lowest value was for the annealed tubing which had the lowest tensile strength. The test at 240 hours at 320C clearly did not predict the longer term data shown in Figure 6-16. The reason for the behavior of the stress relieved tubing remains unexplained.

Creep is affected by composition with the solid solution alloys like tin, oxygen, and niobium having greater effects than the compound-forming elements. The amount of cold work in the last pilger pass also affects creep rate. Higher cold reductions

Figure 6-16



Creep Curves for Zircaloy-4 Tubing Tested Under Internal Pressure at 320C. CWSR is Cold Worked, Stress Relieved. FR is Fully Recrystallized.

Source: ASTM STP 815

produce higher creep rates. Crystal orientation plays a small role with radial textures, producing higher creep rates than circumferential ones.

Irradiation Growth

Growth is defined as a change in shape (usually length for fuel rods) without a volume change during irradiation in the absence of applied stress. Fully recrystallized tubing exhibits less growth under irradiation than does stress relieved tubing. The hexagonal crystal grows less in the "c" direction than in the "a" direction. The mechanisms of growth are intertwined with creep and are poorly understood.

Pellet-Clad Interaction

The fuel failure mechanism generally denoted as pellet-clad-interaction (PCI) can really be a combination of mechanisms. The one most commonly used as a model for study is a crack originating on the inner surface of the tube resulting from a tensile stress set up by hard contact between the fuel pellet or a chip from a pellet and the tube in the presence of an aggressive agent like iodine or cesium. This condition is encountered when there is a rapid power rise in the fuel rod called a ramp.

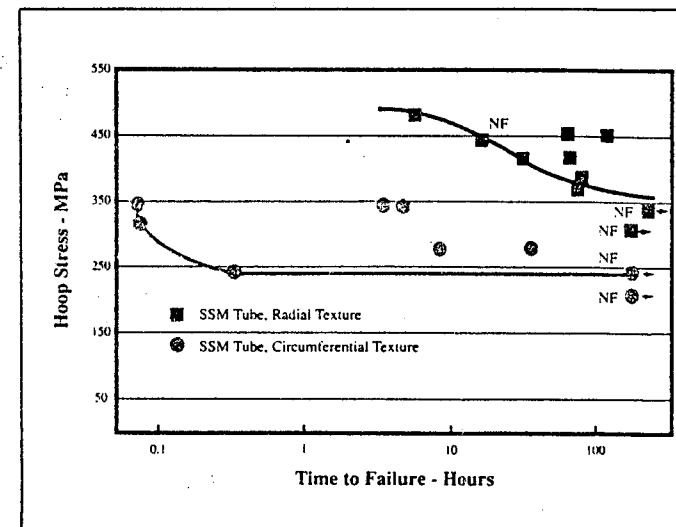
For development purposes, a test using an internal pressure of inert gas containing iodine at some elevated temperature is used to simulate the conditions necessary for crack initiation and growth. The time from the introduction of the iodine to failure at various stress levels is an index of resistance to PCI. At some stress level no failure will occur and this is called the threshold stress for iodine stress corrosion cracking (ISCC).

Work sponsored by the Electric Power Research Institute using cladding especially made for the test series by SANDVIK, explored the effects of inner

surface finish and crystallographic texture on ISCC. They reported in NP 1329 that tubing made with an inner surface that was blasted with abrasives failed at shorter times and at lower stress levels than tubing made with SANDVIK's proprietary flowing acid etch process (see Figure 3-13). Tubes with a radial crystal orientation resisted cracking better than tubes with a circumferential texture as shown in Figure 6-17. They found that the threshold stress for cracking was 40% higher for the radial textured tubing.

The work of Pees and others at KWU, which was published in ASTM STP 681, illustrated the effect of crystal orientation on crack initiation. They prepared a tube by machining it from a piece of plate which had nearly all of the crystals aligned with the basal poles normal to the plate surface. This tube sample had crystal textures around its circumference that ranged from pure radial to pure circumferential as shown in Figure 6-18. The tube was exposed to iodine and internal pressure at an elevated temperature for a short period and then sectioned for study. The density of cracks at

Figure 6-17



Effect of
Crystal Texture
of Tubing on
Resistance to
Iodine Stress
Corrosion
Cracking

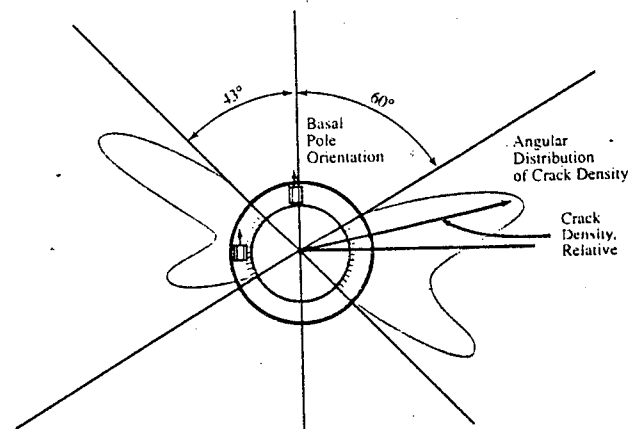
Source:
EPRI NP 1329

each point around the inner surface was determined and plotted as shown in Figure 6-18. The effect of crystal orientation was quite striking. There were no cracks in the regions where the crystals were oriented with their basal poles at an angle of 45 degrees or less to the radial direction. All of the cracks occurred where the crystals had their basal poles closer than 45 degrees to the circumferential direction.

Figure 6-18

Influence of
Crystal
Orientation on
Iodine Stress
Corrosion
Cracking
Resistance

Source:
Peeus et al,
ASTM STP 681



This observation provides an explanation for the excellent resistance to ISCC of SANDVIK's cladding, which is more radial than that produced by other processes, as was illustrated in the cumulative volume fraction plot in Figure 5-15.

There have been two in-reactor "ramp tests" which included SANDVIK's radially textured cladding. In the Studsvik Overramp Project test series, SANDVIK's cladding was noted as G20. It resisted failure at higher ramp levels than the W series cladding, which has a more circumferential crystal texture. In the Fuel Performance Improvement Program sponsored by the Department of Energy, rods made from SANDVIK's standard cladding resisted failure at ramp rates well above those that failed the "reference cladding" and approached the performance of the "barrier cladding" used in BWR's.

References Used in Text

- Andersson, T. and Thorvaldsson, T., "Nodular Corrosion Resistance of Zircaloy-2 in Relation to Second Phase Particle Distribution," ASTM STP 939, 1987, pp. 321-335.
- Andersson, T. and Vesterlund, G., "Beta-Quenching of Zircaloy Cladding Tubes in Intermediate or Final Size - Methods to Improve Corrosion and Mechanical Properties," ASTM STP 754, 1982, pp. 75-94.
- EPRI Report RP 711-1, Babcock and Wilcox.
- Kallstrom, K., Andersson, T. and Hofvenstam, A., "Creep Strength of Zircaloy Tubing at 400°C as Dependent on Metallurgical Structure and Texture," ASTM STP 551, pp. 160-168.
- Kearns, J.J., "Thermal Expansion and Preferred Orientation in Zircaloy," WAPD-TM-472, 1965.
- Kjaer-Pedersen, N. and Woods, K.N., "Ramp Tests On Fuel Rods Containing Solid Pellet, Annular Pellet and Sphere-pac Particle Fuel," Proceedings of American Nuclear Society Topical Meeting on Light Water Reactor Fuel Performance, 1985, pp. 6-35 to 6-51.

- Knorr, D.B. and Pelloux, R.M., "Research on Mechanisms of Stress Corrosion Cracking in Zircaloy," Department of Energy Report DOE/ET/34215-24, June 1981, p. 33.
- Knorr, D.B., Peltier, J.M. and Pelloux, R.M., "Influence of Crystallographic Texture and Test Temperature on Initiation and Propagation of Iodine Stress-Corrosion Cracks in Zircaloy," ASTM STP 824, 1984, pp. 627-652.
- Knorr, D.B. and Pelloux, R.M., "Quantitative Characterization of Crystallographic Textures in Zirconium Alloys," Journal of Nuclear Materials, Vol. 71, 1977, pp. 1-13.
- Marshall, R.P. and Louthan, M.R. Jr., "Tensile Properties of Zircaloy With Oriented Hydrides," Transactions ASM, Vol. 56, No. 3, 1963, p. 693.
- Nagai, N., Kokuma, T. and Fugita, K., "Texture Control of Zircaloy Tubing During Tube Reduction," ASTM STP 754, 1982, pp. 26-38.
- Pees, M., Stehle, H. and Steinberg, E., "Out-of-pile Testing of Iodine Stress Corrosion Cracking in Zircaloy Tubing in Relation to Pellet-Cladding Interaction Phenomenon," ASTM STP 681, 1979, pp. 244-260.
- Schemel, J.H. and McKenzie, R.W., "Pilger Tooling Design for Texture Control," ASTM STP 551, 1974, pp. 169-178.
- Scott, D.B., "Physical and Mechanical Properties of Zircaloy-2 and -4," WCAP-3269-41, Westinghouse Atomic Power Division, May 1965.
- Tenckhoff, E. and Rittenhouse, P.L., "Texture Development and Texture Gradients in Zircaloy Tubing," ASTM STP 458, 1969, pp. 50-67.

- Van Swain, L.F.P., Knorr, D.B., Pelloux, R.M. and Shewbridge, J.F., "Relationship Between Contractile Strain Ratio R and Texture in Zirconium Alloy Tubing," Transactions A, ASM-AIME, Vol. 10A, April 1979, 483-487.
- Wilson, S.A., "Determination of Texture in Zircaloy Using Complete Pole Figures," *Scandinavian Journal of Metallurgy*, Vol. 18, (1989), pp. 67-72.
- "Stress Corrosion Cracking of Zircaloys," EPRI Report NP1329, March 1980.
- "The Studsvik Overramp Project," EPRI Report NP3007, April 1983.

To Dig Deeper

The *Metallurgy of Zirconium* by Ben Lustman and Frank Kerge, Jr., published by McGraw-Hill in 1955 is the original reference, but is now out of print. Douglass prepared a supplement which was published in 1971 by the International Atomic Energy Agency.

The progress of technology of zirconium and its alloys have been chronicled in a series of symposia. The published papers from these meetings provide a good record of the technical work over the last 20 years. Prior to that time much of the work was done in secret by the Naval Nuclear Propulsion Program at the Knolls Atomic Power Laboratory and the Bettis Laboratories operated by Westinghouse. This work is published as reports and is still available in repository libraries.

The first of the open meetings was held in Buffalo, New York by the Electrochemical Society in 1965 and the papers were published in Volume 4, Nos. 3-4, 5-6 and 7-8 of *Electrochemical Technology* in 1966.

The second such meeting was sponsored by Committee B10 of ASTM in 1968 with the papers published as STP 458.

The third meeting was sponsored by the Canadian Metallurgical Society and published in the Canadian Metallurgical Quarterly, Vol. 1, Jan. - Mar. 1972.

Since then Committee B10 of ASTM has sponsored regular symposia on Zirconium in the Nuclear Industry with the papers published as STP's as follows:

1973	STP 551	1982	STP 824
1976	STP 633	1985	STP 939
1978	STP 681	1988	STP 1023
1980	STP 754		

In addition to the symposia volumes, ASTM has published other books on this subject.

STP 368	Corrosion of Zirconium, 1964
STP 639	ASTM Manual on Zirconium and Hafnium, 1977
STP 815	Creep of Zirconium Alloys in Nuclear Reactors, 1982
STP 966	Deformation Mechanisms, Texture and Anisotropy in Zirconium and Zircaloy, 1988

The performance of fuel cladding in nuclear reactors has been documented in a series of American Nuclear Society Topical Meetings on Light Water Reactors. The papers are published by ANS.

1977	St. Charles, MO
1979	Portland, OR
1982	Williamsburg, VA
1985	Orlando, FL
1988	Williamsburg, VA

The Electric Power Research Institute (EPRI) and Atomic Energy of Canada Limited (AECL) regularly publish technical reports relating to zircaloy. These are extremely informative, but too numerous to record in this book. The libraries of both organizations have search capabilities and will generally assist in finding the reports on a particular subject.

English/Metric (SI) Stress Conversion Factors

Look up the stress to be converted in the boldface column:

If in ksi (1,000 psi), read kg/sq mm and MPa in righthand columns.

If in kg/sq mm, read ksi in lefthand column.

Note: 1 MPa (megapascal) = 1 MN per sq m (meganewton per square meter) = 1 N/mm² = 1 MPa = 145.1 psi

0 to 100						100 to 200					
ksi	kg/sq mm	MPa	ksi	kg/sq mm	MPa	ksi	kg/sq mm	MPa	ksi	kg/sq mm	MPa
—	0	—	71.10	50	35.16	344.7	142.20	100	70.32	689.5	213.30
1.42	1	0.70	6.89	72.52	51	35.86	351.6	143.62	101	71.03	696.4
2.84	2	1.41	13.79	73.94	52	36.57	358.5	145.04	102	71.73	703.3
4.27	3	2.11	20.68	75.37	53	37.27	365.4	146.47	103	72.43	710.2
5.69	4	2.81	27.57	76.79	54	37.97	372.3	147.89	104	73.14	717.1
7.11	5	3.52	34.47	78.21	55	38.68	379.2	149.31	105	73.84	724.0
8.53	6	4.22	41.37	79.63	56	39.38	386.1	150.73	106	74.54	730.8
9.95	7	4.92	48.26	81.05	57	40.08	393.0	152.15	107	75.25	737.7
11.38	8	5.63	55.16	82.48	58	40.79	399.9	153.58	108	75.95	744.6
12.80	9	6.33	62.05	83.90	59	41.49	406.8	155.00	109	76.65	751.5
14.22	10	7.03	68.95	85.32	60	42.19	413.7	156.42	110	77.36	758.4
15.64	11	7.74	75.84	86.74	61	42.90	420.6	157.84	111	78.06	765.3
17.06	12	8.44	82.74	88.16	62	43.60	427.5	159.27	112	78.76	772.2
18.49	13	9.14	89.63	89.59	63	44.30	434.4	160.69	113	79.47	779.1
19.91	14	9.85	96.53	91.01	64	45.01	441.3	162.11	114	80.17	786.0
21.33	15	10.55	103.4	92.43	65	45.71	448.2	163.53	115	80.87	792.9
22.75	16	11.25	110.3	93.85	66	46.41	455.1	164.95	116	81.58	799.8
24.17	17	11.95	117.2	95.27	67	47.12	462.0	166.38	117	82.28	806.7
25.60	18	12.66	124.1	96.70	68	47.82	468.8	167.80	118	82.98	813.6
27.02	19	13.36	131.0	98.12	69	48.52	475.7	169.22	119	83.68	820.5
28.44	20	14.06	137.9	99.54	70	49.23	482.6	170.64	120	84.39	827.4
29.86	21	14.77	144.8	100.96	71	49.93	489.5	172.06	121	85.09	834.3
31.28	22	15.47	151.7	102.38	72	50.63	496.4	173.48	122	85.79	841.2
32.71	23	16.17	158.6	103.81	73	51.34	503.3	174.91	123	86.50	848.1
34.13	24	16.88	165.5	105.23	74	52.04	510.2	176.33	124	87.20	855.0
35.55	25	17.58	172.4	106.65	75	52.74	517.1	177.75	125	87.90	861.9
36.97	26	18.28	179.3	108.07	76	53.45	524.0	179.17	126	88.61	868.8
38.39	27	18.99	186.2	109.49	77	54.15	530.9	180.60	127	89.31	875.7
39.82	28	19.69	193.1	110.92	78	54.85	537.8	182.02	128	90.01	882.5
41.24	29	20.39	199.9	112.34	79	55.56	544.7	183.44	129	90.72	889.4
42.66	30	21.10	206.8	113.76	80	56.26	551.6	184.86	130	91.42	896.3
44.08	31	21.80	213.7	115.18	81	56.96	558.5	186.28	131	92.12	903.2
45.50	32	22.50	220.6	116.60	82	57.67	565.4	187.70	132	92.83	910.1
46.93	33	23.21	227.5	118.03	83	58.37	572.3	189.13	133	93.53	917.0
48.35	34	23.91	234.4	119.45	84	59.07	579.2	190.55	134	94.23	923.9
49.77	35	24.61	241.3	120.87	85	59.77	586.1	191.97	135	94.94	930.8
51.19	36	25.32	248.2	122.29	86	60.48	593.0	193.39	136	95.64	937.7
52.61	37	26.02	255.1	123.71	87	61.18	599.9	194.81	137	96.34	944.6
54.04	38	26.72	262.0	125.14	88	61.88	606.8	196.24	138	97.05	951.5
55.46	39	27.43	268.9	126.55	89	62.59	613.6	197.66	139	97.75	958.4
56.88	40	28.13	275.8	127.98	90	63.29	620.5	199.08	140	98.45	965.3
58.30	41	28.83	282.7	129.40	91	63.99	627.4	200.50	141	99.16	972.2
59.72	42	29.54	289.6	130.82	92	64.70	634.3	201.92	142	99.86	979.1
61.15	43	30.24	296.5	132.25	93	65.40	641.2	203.35	143	100.56	986.0
62.57	44	30.94	303.4	133.67	94	66.10	648.1	204.77	144	101.27	992.9
63.99	45	31.65	310.3	135.09	95	66.81	655.0	206.19	145	101.97	999.7
65.41	46	32.35	317.2	136.51	96	67.51	661.9	207.61	146	102.67	1,007.0
66.83	47	33.05	324.1	137.93	97	68.21	668.8	209.03	147	103.38	1,014.3
68.26	48	33.76	331.0	139.36	98	68.92	675.7	210.46	148	104.08	1,021.5
69.68	49	34.46	337.8	140.78	99	69.62	682.6	211.88	149	104.78	1,028.8
71.10	50	35.16	344.7	142.20	100	70.32	689.5	213.30	150	105.49	1,036.1

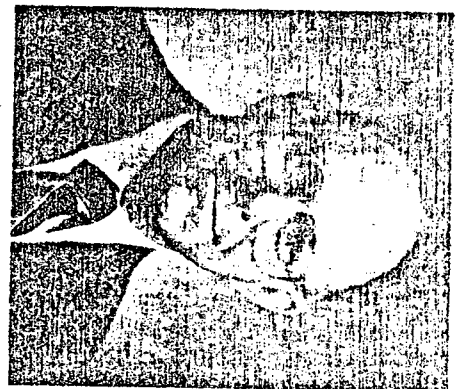
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Temperature Conversions

Albert Sauveur type of table. Look up reading in middle column; if in degrees Centigrade, read Fahrenheit equivalent in right-hand column; if in degrees Fahrenheit, read Centigrade equivalent in left-hand column. Values as printed in "Bethlehem Alloy Steels".

0 to 100				100 to 1000				1000 to 2000				2000 to 3000			
C	F	C	F	C	F	C	F	C	F	C	F	C	F	C	F
-17.8	0	32	10.0	50	122.0	38	100	212	500	932	538	1000	1832	1093	2000
-17.2	1	33.8	10.6	51	123.8	43	110	230	510	950	543	1010	1850	1099	2010
-16.7	2	35.6	11.1	52	125.6	49	120	248	520	968	549	1020	1868	1104	2020
-16.1	3	37.4	11.7	53	127.4	54	130	266	530	986	554	1030	1886	1110	2030
-15.6	4	39.2	12.2	54	129.2	60	140	284	540	1004	560	1040	1904	1116	2040
-15.0	5	41.0	12.8	55	131.0	66	150	302	550	1022	566	1050	1922	1121	2050
-14.4	6	42.8	13.3	56	132.8	71	160	320	560	1040	571	1060	1940	1127	2060
-13.9	7	44.6	13.9	57	134.6	77	170	338	570	1058	577	1070	1958	1132	2070
-13.3	8	46.4	14.4	58	136.4	82	180	356	580	1076	582	1080	1976	1138	2080
-12.8	9	48.2	15.0	59	138.2	88	190	374	590	1094	588	1090	1994	1143	2090
-12.2	10	50.0	15.6	60	140.0	93	200	392	600	1112	593	1100	2012	1149	2100
-11.7	11	51.8	16.1	61	141.8	99	210	410	610	1130	599	1110	2030	1154	2110
-11.1	12	53.6	16.7	62	143.6	100	212	413.6	620	1148	604	1120	2048	1160	2120
-10.6	13	55.4	17.2	63	145.4	104	220	428	630	1166	610	1130	2066	1166	2130
-10.0	14	57.2	17.8	64	147.2	110	230	446	640	1184	616	1140	2084	1171	2140
-9.4	15	59.0	18.3	65	149.0	116	240	464	650	1202	621	1150	2102	1177	2150
-8.9	16	60.8	18.9	66	150.8	121	250	482	660	1220	627	1160	2120	1182	2160
-8.3	17	62.6	19.4	67	152.6	127	260	500	670	1238	632	1170	2138	1188	2170
-7.8	18	64.4	20.0	68	154.4	132	270	518	680	1256	638	1180	2156	1193	2180
-7.2	19	66.2	20.6	69	156.2	138	280	536	690	1274	643	1190	2174	1199	2190
-6.7	20	68.0	21.1	70	158.0	143	290	554	700	1292	649	1200	2192	1204	2200
-6.1	21	69.8	21.7	71	159.8	149	300	572	710	1310	654	1210	2210	1210	2210
-5.6	22	71.6	22.2	72	161.6	154	310	590	720	1328	660	1220	2228	1216	2220
-5.0	23	73.4	22.8	73	163.4	160	320	608	730	1346	666	1230	2246	1221	2230
-4.4	24	75.2	23.3	74	165.2	166	330	626	740	1364	671	1240	2264	1227	2240
-3.9	25	77.0	23.9	75	167.0	171	340	644	750	1382	677	1250	2282	1232	2250
-3.3	26	78.8	24.4	76	168.8	177	350	662	760	1400	682	1260	2300	1238	2260
-2.8	27	80.6	25.0	77	170.6	182	360	680	770	1418	688	1270	2318	1243	2270
-2.2	28	82.4	25.6	78	172.4	188	370	698	780	1436	693	1280	2336	1249	2280
-1.7	29	84.2	26.1	79	174.2	193	380	716	790	1454	699	1290	2354	1254	2290
-1.1	30	86.0	26.7	80	176.0	199	390	734	800	1472	704	1300	2372	1260	2300
-0.6	31	87.8	27.2	81	177.8	204	400	752	810	1490	710	1310	2390	1266	2310
0.0	32	89.6	27.8	82	179.6	210	410	770	820	1508	716	1320	2408	1271	2320
0.6	33	91.4	28.3	83	181.4	216	420	788	830	1526	721	1330	2426	1277	2330
1.1	34	93.2	28.9	84	183.2	221	430	806	840	1544	727	1340	2444	1282	2340
1.7	35	95.0	29.4	85	185.0	227	440	824	850	1562	732	1350	2462	1288	2350
2.2	36	96.8	30.0	86	186.8	232	450	842	860	1580	738	1360	2480	1293	2360
2.8	37	98.6	30.6	87	188.6	238	460	860	870	1598	743	1370	2498	1299	2370
3.3	38	100.4	31.1	88	190.4	243	470	878	880	1616	749	1380	2516	1304	2380
3.9	39	102.2	31.7	89	192.2	249	480	896	890	1634	754	1390	2534	1310	2390
4.4	40	104.0	32.2	90	194.0	254	490	914	900	1652	760	1400	2552	1316	2400
5.0	41	105.8	32.8	91	195.8	260	500	932	910	1670	766	1410	2570	1321	2410
5.6	42	107.6	33.3	92	197.6	266	510	950	920	1688	771	1420	2588	1327	2420
6.1	43	109.4	33.9	93	199.4	271	520	968	930	1706	777	1430	2606	1332	2430
6.7	44	111.2	34.4	94	201.2	277	530	986	940	1724	782	1440	2624	1338	2440
7.2	45	113.0	35.0	95	203.0	282	540	1004	950	1742	788	1450	2642	1343	2450
7.8	46	114.8	35.6	96	204.8	288	550	1022	960	1760	793	1460	2660	1349	2460
8.3	47	116.6	36.1	97	206.6	293	560	1040	970	1778	799	1470	2678	1354	2470
8.9	48	118.4	36.7	98	208.4	299	570	1058	980	1796	804	1480	2696	1360	2480
9.4	49	120.2	37.2	99	210.2	304	580	1076	990	1814	810	1490	2714	1366	2490
				100	212.0	310	590	1094	1000	1832				1093	2000

JOHN H. SCHEMEL



Mr. John H. Schemel, Vice President Research and Engineering, joined Sandvik Special Metals (SSM) in 1975. He is responsible for research, product and process development, equipment and facilities design and construction.

Mr. Schemel received his B.S. in Metallurgical Engineering from Missouri School of Mines and his MBA from the State University of New York at Buffalo. He has had over 25 articles published in various technical journals, as well as the *ASTM Manual on Zirconium and Hafnium* and has coauthored *Ti 3Al 2.5V Seamless Tubing Engineering Guide* which is the leading Titanium Engineering Guide in the aerospace industry. In addition, he holds two patents and he has received the ASTM Award of Merit and the St. Claire de Ville Medal of the Societe Francaise de Metallurgie.