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EVALUATION OF THE ZIRCALOYS FOR
USE IN THE 630A REACTOR

R. K. Betts
630A PROJECT MATERIALS

February 26, 1965

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TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	4
INTRODUCTION	5
USE OF ZIRCALLOY IN OTHER REACTORS	6
DESIGN CONSIDERATIONS FOR THE 630A MARK-V APPLICATION . . .	9
PROPERTIES OF ZIRCALLOY	13
Alloy Development and Composition	13
Structure, Heat Treatment and Cold-Working Characteristics	14
Mechanical Properties of Zircaloy-2 and -4	17
Aqueous Corrosion, Oxidation and Hydriding Characteristics	36
Physical Properties	54
Irradiation Effects	56
OTHER FACTORS CONCERNING THE MARK-V APPLICATION	72
Regulatory Body Approval for Reactor Materials and Construction	72
Joining of Zircaloy to Dissimilar Metals	72
Procurement of Zircaloy-2 and -4	75
Alloys of Zr Containing Nb	76
CONCLUSIONS	77
REFERENCES	78

SUMMARY

Zircaloy-2 and -4 have been evaluated through a literature survey to determine their suitability for use in the 630A Mark V-A and -B cores. On the basis of existing technology, they possess essentially equivalent, adequate mechanical properties and corrosion resistance for the conditions of interest. Either alloy appears suitable for the proposed application.

There may be sufficient data already available to petition for ASME Boiler and Pressure Vessel Code approval of Zircaloy-2. Zircaloy-4, being the newer alloy, has not been used as widely nor evaluated as extensively.

INTRODUCTION

This report presents the conclusions and recommendations from a literature survey concerning the properties and performance of Zircaloy* relative to its potential use in the 630A Mark V reactor.(1) The alloy is under consideration for use as tubing in the calandria-type Mark V-A or center-moderator-type Mark V-B core configuration. Significant savings in fuel cycle costs are possible if Zircaloy is used in these applications instead of, for example, stainless steel. Because of its excellent nuclear characteristics, Zircaloy is used in many contemporary power reactors as fuel cladding and, in some reactors, for water channeling and limited structural application.

The literature on Zircaloy is plentiful and contains many excellent detailed reviews of its development, properties, performance and problems. Some of these reviews are included in the bibliography.(2-9) The development of Zircaloy(10) was the culmination of efforts by several organizations⁺ and it was first used in the nuclear submarines. Its properties are inherently variable for a number of known, and some unresolved, reasons. Many property variances indicated in data summaries are probably due to inequities in control of variables among the numerous test programs rather than from inherent property limitations of the alloy. Although performance data are limited, due largely to the relatively short history of in-reactor application, nonetheless the alloy is of proven technical importance particularly as fuel cladding in water-cooled reactors.

Reviewed in this report are the chemical, physical and mechanical properties of Zircaloy, and the effects of cold-work and irradiation on the latter properties in particular. Also discussed are the inter-related corrosion and hydriding characteristics.

Because the proposed 630A application involves pressure containment, the use of Zircaloy is subject to ASME Boiler and Pressure Vessel Code requirements. No Code approval presently exists or pends; therefore, initiation of a Code Case and ultimate approval is imperative for the present Mark V designs.

*The family of Zr-Sn-Fe-Cr-Ni alloys is implied unless the specific alloy is stated.

⁺Development of the Zircaloys was stimulated in great measure by the Naval Reactors Branch and the Pittsburgh Naval Reactors Office of the U.S. Atomic Energy Commission. Early work resulting in the Zircaloy-1, -2 and -3 compositions was conducted by the U.S. Bureau of Mines (Albany, Oregon), Battelle Memorial Institute, Iowa State College, Argonne National Laboratory, Oak Ridge National Laboratory, Massachusetts Institute of Technology, and the Bettis Atomic Power Laboratory. U.S. Patent Number 2,772,964 is assigned to these alloys. Commercial specifications for Zircaloy-2 and the later Zircaloy-4 alloy are detailed in Mil Z-19859B.

USE OF ZIRCALOY IN OTHER REACTORS

Zircaloy-2 is used principally for fuel cladding in boiling- and pressurized-water reactors.(11) In several reactors it is utilized also for structural applications, such as water channeling and as pressure tubing.(3,12-14) Pressure tube applications of particular interest to 630A include the Canadian Nuclear Power Demonstration Reactor (NPD-II), Douglas Point Nuclear Power Station (CANDU), Carolinas-Virginia Tube Reactor (CVTR), and the Hanford N-Reactor. Prior ASME Boiler and Pressure Vessel Code approval did not necessarily regulate the pressure-containment use of Zircaloy in these four systems. The Code is, of course, not governing in the two foreign reactors, and CVTR and N-Reactor, being experimental, are operated under special legal licensing by the respective states in which they are located.

Table 1 gives a more extensive listing of reactors in which Zircaloy is utilized.

TABLE 1

GENERAL IN-REACTOR USAGE OF ZIRCALOY FOR FUEL CLADDING AND STRUCTURAL APPLICATIONS

Name	Type	Designer	Zircaloy Application	
			Alloy	Component
UNITED STATES				
BCNUS	BWR, SH	General Nuclear	-2	Boiler fuel clad
CVTR	D ₂ O-Coolant	Westinghouse	-4	Pressure tubes, fuel clad
Dresden	BWR	General Electric	-2	Fuel clad, coolant channels
EBWR	BWR	Argonne Nat. Lab.	-2	Fuel clad
Elk River	BWR	Allis-Chalmers	-2	Control rod followers
Hallam	Na-cooled	Atomics Int'l.	-2	Water process tubes
HRE-II	D ₂ O-Homogeneous	Oak Ridge Nat. Lab.	-2	Core vessel
Indian Point	PWR	Babcock & Wilcox	-2	Coolant channel
N-Reactor	PWR	Hanford	-2	Pressure tubes
Pathfinder	BWR, SH	Allis-Chalmers	-2	Boiler fuel clad
Savannah, NS	PWR	Babcock & Wilcox	-2	Coolant channels
Shippingport-I	PWR	Westinghouse	-2	Fuel clad and matrix
Shippingport-II	PWR	Westinghouse	-4	Blanket fuel clad
VBWR	BWR	General Electric	-2	Fuel clad
Yankee	PWR	Westinghouse	-2	Control rod followers

TABLE 1
(Cont)

Name	Type	Designer	Zircaloy Application	
			Alloy	Component
FOREIGN				
CANDU	D ₂ O- Cooled	Canadian GE/AECL	-2	Fuel clad, pressure tubes
JPDR	BWR	General Electric	-2	Fuel clad, channels, followers
Kahl/Main	BWR	General Electric	-2	Fuel clad, channels
NPD-II	D ₂ O-Cooled	Canadian GE/AECL	-2	Fuel clad, pressure tubes
R-3/ADAM	D ₂ O- Cooled	Swedish AEC	-2	Fuel clad

1
∞
1

DESIGN CONSIDERATIONS FOR THE 630A MARK V APPLICATION

Two alternate core configurations are proposed for the 630A Mark V Nuclear Steam Generator.(1,15) The "A" design is a version of the calandria-type moderator water container from previous cores.(16) Tubes extend through the calandria, as shown in Figure 1, attached by suitable seal-joints to the upper and lower tube sheets and contain the fuel elements in the primary coolant flow path. The "B" concept locates water containment tubes centrally in each fuel element cluster or cell, with tubes joined to the shield plug bottom header. This is illustrated in Figure 2. Fuel element design features of both proposals provide insulation for the Zircaloy from direct exposure to the high coolant-gas temperature. Table 2 presents some of the pertinent environmental and operational factors common to both configurations.

TABLE 2

ENVIRONMENTAL AND OPERATIONAL FACTORS FOR ZIRCALOY IN THE MARK V DESIGNS

<u>Environmental Exposure</u>	<u>Operating Conditions</u>
<u>Water Side</u>	<u>Design Life</u>
Moderator water at 235° to 255°F, flowing	20 years
<u>Primary Coolant Side</u>	<u>Stress</u>
Helium, insulated from hottest gas flow	ASME Boiler and Pressure Vessel Code allowable
<u>Neutron Dosage</u>	<u>Design Pressure</u>
2.25 x 10 ²² nvt (> 1 Mev) at 61.5 MW and 70% utilization	900 psi
	<u>Operating Pressure</u>
	575 psi { 825 psig coolant (250. psig water) }
	<u>Metal Temperature</u>
	450°F maximum

Significant differences exist in the manner by which tubes are joined either to the calandria tube sheet or to the shield plug bottom header. In both instances, the joint is between dissimilar

Fig. 1 - Calandria-type reactor design for the 630A Mark V(A).
(221R441)

Fig. 2 - 630A Mark V(B) Reactor-Shield Plug Assembly (221R466)

metals, e.g., Zircaloy to Incoloy 800. In the "B" concept, it is proposed to use either a bolted, O-ring-sealed hub or a conventional rolled joint of the tube to the plug head, and the moderator tube would be all Zircaloy.

The "A" design, on the other hand, can utilize neither a rolled joint nor a flange seal because of insufficient ligament thickness in the calandria tube sheet. A welded seal is the alternative method; however, sound welds cannot be obtained between Zircaloy and the dissimilar tube sheet metal. The design, therefore, incorporates a bi-metal tube of Zircaloy with, for example, Incoloy 800 nozzles. Two techniques have been used successfully on an experimental basis to form the bi-metal joint necessary for this application. They are explosive forming and tandem extrusion. Although both are apparently feasible, these processing methods have not yet been applied in significant service applications. Tube joints are, however, being evaluated by GE-APED, SRL, AECL, GNEC, Bettis, KAPL, CVNA and others. The use of a bi-metal tube injects additional requirements for a Code Case approval.

PROPERTIES OF ZIRCALOY

Of the common structural metals having low neutron cross sections, viz., Al, Be, Mg and Zr, only the latter has a suitable combination of inherent corrosion resistance, mechanical strength and physical properties at temperatures which exist in water environment power reactors. The properties of unalloyed crystal bar and sponge Zr are, however, somewhat variable being particularly sensitive to nitrogen and oxygen content, and to hydriding. The potential reward of neutron economy gave impetus to the development effort which culminated in the Zircaloy series of alloys which possess significantly improved corrosion resistance and mechanical properties over unalloyed Zr.

Because of its nuclear attractiveness, Zircaloy-2 has been subject to evaluation by many investigators following its inception in 1953, and much property data are available. The variances evident in its mechanical properties, and the uncertainties which exist in the long-time effects of hydriding and irradiation are not surprising for a material so contemporary when compared to ferrous alloys. For example, the technology of making Zircaloy pressure tubing was virtually non-existent before 1957.(17) The summary presented here is believed to embody the most recent understanding of this material, the technology of which is advancing rapidly.

Alloy Development and Composition

The elements Cr, Fe, Ni and Sn were found to be most effective in stabilizing and enhancing the properties of Zr.(10) For example, 1.5% Sn* effectively offsets the deleterious corrosion effect of up to 1000 ppm nitrogen, also, to a lesser extent, the similar effect of carbon and aluminum on corrosion resistance. Zircaloy-1, an alloy of sponge Zr with 2.5% Sn, marked a significant improvement in the corrosion resistance of Zr, but was precluded by the superior Zircaloy-2 alloy.

In the development of Zircaloy-2, Cr alone or with Sn imparted high temperature water and steam corrosion resistance to Zr, but the quantities necessary produced undesirable hardening. Ni or Fe with Sn were also singly effective, and equal to each other, at producing high temperature corrosion resistance in Zr without undue hardening. Both in combination with Sn were more corrosion-enhancing than Cr with Sn. A balance of corrosion resistance, fabricability and strength was achieved by the comparison of all four elements with Zr, designated Zircaloy-2.

*Compositions in weight percent unless otherwise stated.

Zircaloy-3 was an attempt to improve on the already very successful Zircaloy-2 alloy, but it only equalled the corrosion resistance of Zircaloy-2 and was 25 percent weaker. It was, in actuality, three alloys of Zr with Sn and either Ni or Fe or both without the strengthening benefit of Cr as previously described.

Fuel cladding experiments began, as time passed, to reveal some loss of metal properties due to hydrogen absorption. When studies showed that Ni enhanced the absorption of hydrogen in the alloys, the Zircaloy-2 composition was re-evaluated with respect to Ni. The effect of coolant chemistry was also studied. Nickel-free Zircaloy-2 and ultimately Zircaloy-4 resulted from the alloy program.

Simply eliminating Ni from Zircaloy-2 effectively reduces its propensity for hydrogen absorption in water and steam, but impaired its corrosion resistance in steam at 750°F and above. Zircaloy-4, made by adding additional Fe to compensate for the absence of Ni in the modified Zircaloy-2 formula, retained good corrosion resistance even at 750°F and above, but hydrogen absorption was lessened only at sub-critical water temperatures.

The compositions of Zircaloy-2, nickel-free Zircaloy-2, and Zircaloy-4 are given in Table 3.

It should be recalled that these alloys were being developed for fuel cladding in power reactors where very high temperature water (680°F) and superheated steam (to 850°F) were desirable for thermal efficiency. The foregoing conclusions are, therefore, for conditions under which the performance of the alloys is very sensitive to temperature, composition, and processing history. The conclusions do not apply at the relatively low 630A temperature where, as will be shown, corrosion rates and associated hydrogen uptake are quite low. In other words, either Zircaloy-2 or -4 should be adequate in terms of resistance to corrosion and hydriding under the more moderate 630A conditions.}}

Structure, Heat Treatment and Cold-Working Characteristics

The Zircaloys, like the base metal Zr, have a close-packed hexagonal crystal structure.^(4,7,18,19) The alpha (α) structure in Zircaloy-2 obtains up to approximately 1480°F, where a change to body-centered cubic begins. Transformation to the beta (β) structure is complete at approximately 1820°F, and this phase exists to the melting point, 3360°F. Figure 3 is a portion of the Zr-Sn equilibrium diagram showing the principal regions of α , β and $\alpha + \beta$. Transition temperatures are affected by heating and cooling rates. Minute amounts of intermetallic compounds of the principal alloying

TABLE 3
MAJOR ALLOYING CONSTITUENTS OF ZIRCALOY-2,
NICKEL-FREE ZIRCALOY-2, AND ZIRCALOY-4

Alloy	Alloying Addition*	Concentration Range (w/o)	Nominal Concentration (w/o)
Zircaloy-2	Sn	1.20-1.70	1.5
	Fe	0.07-0.20	0.13
	Cr	0.05-0.15	0.10
	Ni [†]	0.03-0.08	0.05
Nickel-Free Zircaloy-2	Sn	1.20-1.70	1.5
	Fe [‡]	0.12-0.18	0.15
	Cr	0.05-0.15	0.10
	Ni	0.007 max	0.005
Zircaloy-4	Sn	1.20-1.70	1.5
	Fe [‡]	0.18-0.24	0.21
	Cr	0.07-0.13	0.10
	Ni	0.007 max	0.005

*The remaining constituent of all three alloys is sponge zirconium with the following maximum impurity levels (in ppm); Al, 75; B, 0.5; Cd, 0.5; C, 270; Co, 20; Cu, 50; Hf, 200; H, 25; Pb, 130; Mg, 20; Mn, 50; N, 80; Si, 120; Na, 20; Ti, 50; and W, 100.

[†]Nickel content distinguishes the Zircaloy-2 composition from the other two alloys.

[‡]Iron concentration differentiates between nickel-free Zircaloy-2 and Zircaloy-4.

FIG. 3 - Partial diagram of zirconium-tin system (after D. J. McPHERSON and M. HANSEN⁷⁸)

elements, viz., Zr_4Sn , Zr_2Ni , $ZrFe_2$ and $ZrCr_2$ (and certain impurities), exist in the α -phase at reactor temperature; thus, the alloy is only pseudo single-phase. Physical properties and environmental corrosion resistance are affected by the phase regions, heating time and quenching rates of various heat treatments.

Prismatic slip ($10\bar{1}0$ planes) and twinning are the major modes of deformation at low temperature, with possible basal and pyramidal plane slip after heavy deformation.(2,20,21) The asymmetry of prismatic slip renders the alloy susceptible to preferred orientation during fabrication and marked anisotropy (directionality) of mechanical properties, e.g., ratios of 1-1/2 to 2 in percent elongation. Zircaloy may be cold-worked with resulting strengthening and hardening. Recrystallization can be obtained in 30 minutes at 1020° to 1065°F. Providing the surface is to be removed by machining, annealing can be accomplished in air at 1500° to 1600°F in 15 minutes for 0.2-inch section thickness. Longer times for heavier sections, as in standard "base annealing" practice (20 hours at 1380°F), require use of inert atmospheres or vacuum equipment. Vacuum annealing effectively lowers the hydrogen content.

Figure 4 illustrates the effect of several percentages of cold-work on Zircaloy-2 hardness, and shows the onset of recovery after 1000 hours at various temperatures beginning with 570°F.(20) The annealed hardness of Zircaloy-2 is about 90 Rockwell-B. Effects of cold-work and annealing on anisotropy are presented in the section on mechanical properties.

Grain growth reportedly does not occur in Zircaloy-2 below 1200°F. Contrasting results are reported with regard to whether or not aging occurs.(20,21) The effect on strength where aging is reported to occur, is small and not of much consequence below 680°F.

The principal heat treatments for Zircaloy involve soaking and quenching from the β -phase field, annealing in the α regions, and pre-filming by steam autoclave. These treatments significantly affect corrosion and hydriding behavior.(10)

Mechanical Properties of Zircaloy-2 and -4

Excellent detailed presentations of the mechanical properties of Zircaloy-2 are contained in References 2 through 9 and 22 and on Zircaloy-4 in Reference 14. Representative data have been extracted from among these and are included herein. Although few references contain comparative data of Zircaloy-2, -4, or the nickel-free Zircaloy-2, it is stated in several that no differences exist in the mechanical properties of Zircaloy-2 and -4, presuming generally that the amount of interstitials in each is virtually equal.(4,7,14)

FIG. 4 -

The Effect of 1000 hr Annealing in Helium from 300 to 700 C (572 to 1292 F) on the Hardness of Cold-Worked Zircaloy-2

Increased strength results from cold-working Zircaloy-2, and Canadian designers utilize cold-worked material for the NPD-II and CANDU reactors. ASME Boiler and Pressure Vessel Codes do not permit cold-work properties in stress allowances, thus the 630A design and Code Case petition will be based on annealed properties. Data presented here are for annealed metal; however, some effects of cold-work are included for general interest.

The mechanical properties of Zircaloy are also significantly affected by its inherent anisotropy, by irradiation, and by hydride precipitation or other interstitial contaminants.

One factor of considerable importance to the study of Zircaloy is the recent correlation of the orientation effect of hydride-precipitate (platelets) on mechanical properties.(23) Although not widely confirmed,(24) it was demonstrated that precipitates, greater than a certain length, oriented perpendicular to an applied stress significantly lower the tensile properties. Alignment with the stress seems not to affect strength. This discovery may be the reason for the variations in the literature on Zircaloy properties. Some existing data summaries may require complete re-evaluation to take into account hydride orientation.(25,26)

Tensile Strength - Table 4 presents a summary of representative tensile data for annealed Zircaloy-2, as compiled from several sources in Reference 7. Figures 5 and 6 illustrate graphically some transverse and longitudinal tensile property relationships for the alloy as a function of temperature.(4)

Annealed Zircaloy-4 tensile data are shown in Figures 7 and 8.(14) Specimens were from tubing prepared for in-reactor corrosion loop tests in early phases of the CVTR study program. Similar data from tests conducted on the actual power plant pressure tubes are presented in Figures 9 and 10.(14) Data from these curves were the basis for the design stress allowances used in the CVTR.

Some effects of cold-work on tensile properties of Zircaloy-2 are illustrated in Figures 11 and 12.(4)

Figure 13 illustrates typical stress-strain curves for annealed and cold-worked Zircaloy-2 tested at 535°F.

Allowable Stress Intensity - For design purposes, the allowable stress intensity of a material must be based on annealed properties to comply with the ASME Boiler and Pressure Vessel Code. Figure 14 presents a compilation of two design stress intensity curves for Zircaloy-2 in comparison with the established Code allowable stress for Type 304 stainless steel.(27) Canadian designers established the higher curve of allowable stress intensity based on one-third ultimate tensile strength of Zircaloy-2 for the CANDU and NPD-II pressure tubes.(15) The criteria used to develop the one-third

TABLE 4 Tensile Properties of Unirradiated Zircaloy-2
(Annealed 1450 to 1550°F)

	Room Temperature		300°F		600°F		800°F		1000°F		1200°F
	Long. ^a	Trans. ^b	Long.	Trans.	Long.	Trans.	Long.	Trans.	Long.	Trans.	Long.
Ultimate strength, 1000 psi	67.8±5.1	68.4±2.5	49	43	33.7±2.3	30.9±2.1	28	22	19	16	13.2
0.2% offset yield strength, 1000 psi	41.3±5.5	58.6±3.5	27	37	15.8±1.2	21±2.5	14	17	11	14	6.4
Reduction of area, %	40	55	55	65	65	78	84	85	88	88	---
Total elongation, %	26±3	34±5	32	40	46±5	38±6	28	20	45	40	80
Uniform elongation, %	15	11	16	23	20	15	16	6	13	8	---
Young's modulus (dynamic tests), 10 ⁶ psi	13.7	---	12.5	---	11.0	---	10.1	---	9.1	---	---

^a Longitudinal
^b Transverse

Note: Data shown are average values; one standard deviation is added where available.

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FIG. 5 - Effect of Temperature on Longitudinal Tensile Properties of Annealed Zircaloy-2.

FIG. 6 - Effect of Temperature on Transverse Tensile Properties of Annealed Zircaloy-2.

FIG. 7 - Zircaloy-4 In-Pile Loop Pressure Tube Tensile Properties

FIG. 8 - Phase II Zircaloy-4 Pressure Tube Tensile Properties

FIG. 9 - Zircaloy-4 CVTR Plant Pressure Tube
Tensile Properties - Ultimate Strength

FIG. 10 - Zircaloy-4 CVTR Plant Pressure Tube Tensile Properties
0.2% Yield Strength

FIG. 11 - Tensile Properties of Zircaloy-2 as a Function of Cold Work and Temperature.

FIG. 12 - Ductility of Zircaloy-2 as a Function of Cold Work and Temperature.

FIG. 13

FIG. 14

ALLOWABLE STRESS INTENSITY
VS.
TEMPERATURE
ZIRCALOY 2 and 304 S.S.

SEE 2/25/64

ultimate tensile strength curve are similar to those used in the ASME Code, a principal difference being the quantity of data used to determine the ultimate strength.

CVTR pressure tube designs were based on a one-third ultimate tensile strength allowable stress of 18,000 psi at 250°F.(4) NS Savannah fuel element holders were designed on the basis of a primary membrane stress (S_m) of 17,600 psi at 600°F [two-third average yield strength].(13)

Modulus of Elasticity - Figure 15 is a comprehensive plot of elastic modulus data from annealed Zircaloy-2 longitudinal and transverse specimens, and for cold-worked material.

Poisson's Ratio - Some data available on this property for Zircaloy-2 are given in Table 5.(4)

TABLE 5
POISSON'S RATIO FOR ZIRCALOY-2

<u>Specimen Condition</u>	<u>Test Temperature, OF</u>	<u>Poisson's Ratio</u>	<u>Related Modulus of Elasticity, 10⁶ psi</u>
Annealed	80	0.368-0.380	13.9-14.3
	300	0.425-0.460	13.3-13.8
Cold-Worked	80	0.382-0.406	14.5
	300	0.392-0.432	13.9-14.2

Creep Strength - Creep tests of annealed Zircaloy-2 indicate a critical stress sensitivity at 550°F.(7) A stress of 22,500 psi reportedly caused low secondary creep rate in 15,500 hours, but a small increase in stress caused short-time rupture. At 550°F, 15,200 psi resulted in 1% deformation in 10,000 hours. The primary creep strain appears typically stress sensitive and, likewise, secondary rates seem temperature sensitive. Figures 16 and 17 illustrate primary and secondary creep characteristics of the alloy.(4)

Figure 18 shows a curve of comparative creep data for annealed Zircaloy-2 and -4 tested at 662°F.(14) Figures 19 and 20 present summaries of Zircaloy-2 creep data in master curves of rupture and creep times and stresses incorporating Larson-Miller parameters. Design points of the CVTR are shown on the curves.

For long-term structural applications, it is necessary to know the time-temperature-stress dependency of the initiation of third stage creep. Figure 21 shows some data of this type.(4)

FIG. 15 - Modulus of Elasticity of Zircaloy-2 as a Function of Temperature.

FIG. 16 - Primary Creep Strain of Zircaloy-2.

FIG. 17 - Secondary Creep Rate of Zircaloy-2.

- Zircaloy-2 base annealed 20 hrs. at 750°C
- + Zircaloy-4 base annealed 20 hrs. at 750°C
- Zircaloy-4 mill annealed 15 min. at 843°C

FIG. 18 - Creep of Zircaloy-4 at 350°C

FIG. 19 - Master Rupture Curve of Annealed Zircaloy-2

FIG. 20 - Master 1% Creep Curve of Annealed Zircaloy-2

FIG. 21 - Time for Onset of Third-Stage Creep in Zircaloy-2.

Impact Strength - Figure 22 shows Charpy impact data for Zircaloy-2 with horizontal and vertical notch variations. Unhydrided Zircaloy exhibits notch ductility at room temperature and above. Studies of fracture characteristics show that, when it occurs, fracture proceeds by nucleation of small cracks.(4) It is not subject to catastrophic failure by propagation of single large cracks as are ferritic steels.

Fatigue Strength - Stress-fatigue data are shown in Figure 23 for Zircaloy-2 and -4.(4,14) Both are notch sensitive, but Zircaloy-4 possesses the higher stress tolerance for cycles-to-failure. Figure 24 illustrates the effect of notch geometry in the range of $K_T = 1$ to 9 (theoretical stress concentration factor) on fatigue life of Zircaloy-2. Combined static and alternating stresses decrease the fatigue strength of Zircaloy-2, as shown on the modified Goodman diagram of Figure 25.

The strain-fatigue properties of Zircaloy-2 appear from the literature to be insensitive to temperature, orientation and K_T .

Aqueous Corrosion, Oxidation and Hydriding Characteristics

Reaction rates of the Zircaloys with oxygen and hydrogen are extensively documented,(3-5,10,14,28-31) and recently some specific mechanisms have been postulated.(31,32) The aspect of hydrogen absorption is of particular significance from the deterioration it may produce in mechanical properties. Most important in this respect is the striking interplay of oxidation and the rate of hydriding. A very small quantity of oxygen in the reactive environment drastically reduces the amount of hydrogen absorbed. Oxidation rate is reportedly independent of the oxygen source, i.e., gas-phase or aqueous corrosion.(32,34)

Although the 630A reactor primary coolant, helium, is in itself inert, the presence of hydrogen as a contaminant could result in serious hydriding. The presence of oxygen gas or water vapor could be beneficial.(35)

Corrosion and Oxidation Processes - The Zircaloys derive corrosion (oxidation) protection from the formation of a stable surface layer of ZrO_2 in an environment containing sufficient oxygen,(18) generally:

or

Most importantly, the oxide can be substoichiometric, i.e., $ZrO_{1.9}$, in the early stages of formation and retain a stoichiometry gradient as the film thickens. Specific mechanisms governing both the corrosion and hydriding characteristics have recently been attributed to this gradient and the anion vacancy paths associated with it.(32,33)

FIG. 22 - Charpy Impact Data on Zircaloy-2.

FIG. 23 - Reverse Bend Fatigue of Zircaloy-2 and Zircaloy-4

FIG. 24 - Results of Reverse-Bend Fatigue Tests at 600°F and Zero Mean Stress on Base-Annealed Zircaloy-2.

FIG. 25 - Modified Goodman Diagram Showing the Combined Static and Bending Fatigue Test Results at 600°F for Zircaloy-2.

Corrosion of Zircaloy is characterized by two distinct rates, usually referred to as pre- and post-transition. The transition "point", observable as a time-temperature dependent phenomenon, is believed to indicate a breakdown of the original oxide film and the alteration of rate controlling factors. The transition event may be hastened by mechanical and/or thermal stresses superimposed on the natural film-growth stresses of the initial film.

Pre-transition corrosion normally follows a quasi-cubic law, rate controlled by oxygen diffusion and thickness change in the scale. The rate decreases with time as the surface oxide layers approach the di-oxide composition leaving fewer oxygen (anion) vacancies and slowing the diffusion of oxygen to the substoichiometric inner layers. Corrosion is not affected by pH 10.0 to 11.3 in the presence of LiOH or by neutral pH maintained by NH_4OH . Concentration in crevices must be avoided by suitable design.(5,38) Fluoride ion at approximately 10 ppm concentration seriously increases corrosion and hydrogen pickup.

Post-transition corrosion rates are postulated as being a combined effect of continued protection by the original bulk oxide layer plus rapid oxidation of metal (or at least low stoichiometry sub-layers of oxide) exposed by cracking of the original oxide.

Hydriding Processes - Empirical studies show that gross hydriding results from the presence of atomic hydrogen (H^0) rather than the molecular form (H_2) in the corrosion environment.(28) Recent proposals have related the mechanisms of hydriding to the same anion vacancies which control oxidation.(32,33) Charged protons (H^+) form when water is dissociated by the takeup of an oxygen anion (O^{2-}) at an oxide surface vacancy site. Electrons liberated by the general vacancy interaction neutralize the protons to form hydrogen atoms. Thence, the atoms may either combine into H_2 or enter and migrate through the oxide by virtue of the anion vacancies. Here the controlling mechanism is postulated as the physical size relationship of the hydrogen atoms and the vacancy paths, the atoms being smaller than a vacancy. Driven inward by the concentration gradient, atoms reach the metal interface where absorption or chemical hydriding occurs depending on temperature and hydrogen concentration.

Corrosion and Hydriding Rates - Figures 26 through 29 illustrate some aqueous corrosion rates and transition effects for Zircaloy-2 and -4 as a function of exposure temperature and prior heat treatment.(31) The expressions

$$X_f = 0.00252 W \quad (3)$$

for calculating film thickness (X_f in mils) from weight gain (W in mg/dm^2), also the relation

$$X_m = 0.00158 W \quad (4)$$

for metal penetration (X_m in mils) from the weight gain may be used to relate corrosion to the indicated surface effects.(4)

CORROSION OF ZIRCALLOY - 2 ALPHA

(Negative No. 35046-8)

FIG. 26 -

CORROSION OF ZIRCALLOY - 2 BETA QUENCHED

FIG. 27 -
(Negative No. 35046-9)

(Negative No. 35046-5)

FIG. 28 -

FIG. 29 -
(Negative No. 35046-2)

Metal penetration in 7300 days (20 years) would be about 4.7×10^{-5} inch for either Zircaloy-2 or -4 at 500°F, 30 mg/dm² weight gain.

Extrapolating the transition time as a function of temperature, as in Figure 30, indicates that at the 630A temperature of 450°F the transition phenomenon should not occur during predicted reactor operation. From these curves (Figures 26 through 30) general corrosion effects seem negligible for the predicted operation with a comfortable margin to 550°F.

Hydrogen uptake in the Zircaloys in water is a function of the corrosion rate. Approximately 20 to 30 percent of the atomic hydrogen produced by the decomposition of water is absorbed by the metal. Zircaloy-4 possesses a distinct advantage over Zircaloy-2 in absorbing hydrogen at a lower rate in high temperature water, and nickel-free Zircaloy-2 is better than both, Figure 31.

Figures 32 through 35 show the results of summary of data for hydrogen uptake in Zircaloy-2 and -4 tested in various heat treatment conditions. These 550°F temperature relationships are in themselves extrapolations, but could be assumed as being "worst-case" conditions for the 450°F 630A application. Beta-quenched Zircaloy-4 shows the lowest hydrogen pickup rate, about 50 to 100 ppm in 7000 days for 20-mil material corroded from one side.

It is the precipitated hydride in Zircaloy that causes the effects on properties. For this reason, the solubility of hydrogen in the α -phase of the alloy is of interest. Figure 36⁽³⁷⁾ illustrates this terminal solubility as a function of temperature. This curve shows, by extrapolation, that the α -phase of the alloy has a solubility limit of about 20 ppm of hydrogen at the proposed 630A temperature of 450°F. Vacuum annealed Zircaloy can have a starting concentration of 8 ppm hydrogen. Pre-filming treatments conducted in steam autoclaves at 750°F will add another 2 to 5 ppm for a total of 10 to 13 ppm before service use begins. Adding the equivalent hydrogen pickup for Zircaloy-4 during 7000-day corrosion at 500°F, the material could contain as much as 90 ppm hydrogen above saturation. It has been reported that at least 500 ppm of hydrogen has no serious effect on properties of Zircaloy-4 at 300°F.⁽¹⁴⁾ Zircaloy-2 would contain about twice the hydrogen for the same amount of corrosion, but no significant effects on properties are reported for at least 250 ppm of hydrogen.⁽³⁾ Except for localized effects due to concentration of hydrogen into colder metal areas by diffusivity mechanisms, unknown localized corrosion effects in service, or hydriding during fretting, either alloy probably would perform satisfactorily.

FIG. 30 - Transition time for corrosion of Zircaloy-2 in water and steam (750°F)

FIG. 31 - Hydrogen Pick-Up for Three Types of Zircaloy

ZIRCALOY - 2 ALPHA

FIG. 32 -
(Negative No. 35046-7)

FIG. 33 -
(Negative No. 35046-4)

FIG. 34 -
(Negative No. 35046-3)

FIG. 35 -
(Negative No. 35046-6)

SEM-LOGARITHMIC 359-B
KELFEL & ESSER CO.
4 CYCLES X 70 DIVIS ONS
MADE IN U.S.A.

HYDROGEN SOLUBILITY, ppm by weight

TEMPERATURE, °F

1540 1000 750 540 450

$1/T \times 10^4, ^\circ F$

FIG. 36 - Terminal solubility of hydrogen in alpha-phase of Zircaloy-2 (37)

Exposed to the helium atmosphere of the primary-coolant environment, Zircaloy will obviously not corrode. However, unfilmed Zircaloy will absorb significant amounts of hydrogen even as low as 210°F, and the presence of hydrogen as a contaminant in the primary-coolant helium could produce catastrophic hydriding at 300°F in a few days.(35) Pre-formed oxide films offer only transitory protection and an oxidizing environment must obtain to minimize hydriding. One or both of the following steps appear to be in order for protection against hydriding on the primary-coolant side:

- A. Continuously purify the helium with hydrogen getters.
- B. Maintain a small concentration of oxygen (~ 0.1 vol.%) to maintain the protective metal oxide film.

Although the reaction rate of Zircaloy with nitrogen is very slow at 450°F and below(18) concentration should be minimized by gettering to prevent possible loss of corrosion resistance.

Component Pre-Service Filming and Corrosion Test - The dense, black oxide film on Zircaloy has been shown to be advantageous toward decreasing further oxidation and lessening hydrogen absorption. A pre-service operation is performed on Zircaloy components exploiting this film characteristic by developing an initial oxide layer. Importantly, the operation also serves as a quality control check for ultimate corrosion resistance of the material.(14) The finished component is exposed in an autoclave to high temperature water (650°-680°F) or steam at 750°F for 72 hours. This exposure not only establishes the initial protective film, but it has been shown to disclose inherent corrosion resistance deficiencies in the material by the presence of white, flaky oxide. Studies have been conducted on a similar procedure conducted in pure oxygen.(34) Similar oxide filming and quality control are achieved; however, the absence of hydrogen is a distinct advantage.

Fretting Corrosion - Fretting is an attrition of metal between two contacting surfaces which are vibrating with small amplitudes and loads in the absence of a corrosive environment and during which action the parts are not out of contact. In this sense it is not unlike abrasive wear. Practically, though, in-reactor the presence of a flowing corrosive media and unknown patterns of relative motion of components subject to fretting, may create serious localized damage by continued flushing and reoxidizing of the area. An investigation of Zircaloy-2 tubing in the PRTR showed that after only two months, 1600 corrosion areas were observed, 2.2 percent were deeper than 0.010 inch, and maximum penetration was 0.026 inch.(39) Ex-reactor tests showed severity of fretting to be a direct function

of increased environment temperature, increased vibration (frequency) and increased clearance. Although deep corrosion might be eliminated by careful design, hydriding may occur even in areas of shallow corrosion due to the continued removal of the protective oxide film.⁽⁴⁰⁾

NRX reactor tubes exhibited no serious fretting corrosion in three years of operation.⁽³⁾ The Canadian reactor incorporates wire mesh bearing pads to reduce the possibility of fretting.

Impact Corrosion - Lobsinger reports⁽⁴¹⁾ on a phenomenon observed in Hanford studies. A plunger tipped with Zircaloy-2 was repeatedly impacted 550 times per minute against a plate of the same alloy using about 2 inch-pound of energy. Measurements of plunger wear showed losses of 2.5 and 7 mils, respectively, in 570°F and 750°F deionized water for a period of three weeks. This test implies that any repetitive impact due, for example, to gross ship motion, may be such as to cause accelerated corrosion of reactor components.

Physical Properties^(18,19,42)

Nuclear Cross Section - The macroscopic nuclear cross section (Σ) of Zircaloy-2 is 0.0086 cm⁻¹ ($\sigma_{\text{abs}} = 0.22$ to 0.24 barns/atom).

Density - The density of hot-rolled, vacuum annealed Zircaloy-2 is 6.570 gm/cc (0.237 lb/in³).

Melting Point - The melting point of Zr metal is 1855° ± 15°C.

Specific Heat - The specific heat of Zr metal at room temperature is 0.0692 cal/gm and at 127°C it is 0.0739 cal/gm. Specific heat in the range of 1.2° to 4.2°K may be calculated by the formula:

$$C_p = 6.92 \times 10^{-4} T_{\text{OK}} + 464.5 \left(\frac{T}{265} \right)^3 \text{ cal/mol-}^\circ\text{C}$$

Thermal Expansion - For annealed Zircaloy-2 the thermal expansion equations are as follows:

$$L_t = L_o (1 + 4.62 \times 10^{-6} \Delta T) \quad \text{parallel to rolling}$$

$$L_t = L_o (1 + 3.71 \times 10^{-6} \Delta T) \quad \text{normal to rolling}$$

$$L_t = L_o (1 + 6.58 \times 10^{-6} \Delta T) \quad \text{transverse to rolling}$$

$$\Delta T = T - 30^\circ\text{C}$$

Figure 37 is a plot of the instantaneous and average coefficients of thermal expansion as a function of temperature.

FIG. 37

Thermal Conductivity - Figure 38 is a graph of the thermal conductivity of Zircaloy-2 from room temperature to 1100°F.

Electrical Resistivity - The resistivity for Zircaloy-2 at room temperature is $74 \mu \Omega\text{-cm}$.

Latent Heat - The latent heat of fusion for Zr metal is 5.5 Kcal/mole.

Irradiation Effects

Zircaloy has been evaluated and irradiation effects summarized for short-time test programs and fuel clad studies. (2-7,14,20,24,42-45) No significant history of experience is as yet available for components such as pressure tubes. Irradiation affects the mechanical properties of Zircaloy in the typical manner of increasing strength and decreasing ductility and impact resistance. Some effects on corrosion and hydrogen pickup have also been observed, but these are not clearly defined as irradiation-induced, per se, as opposed to uncertain in-reactor coolant environment.

Tensile Strength - The results of post-irradiation studies of Zircaloy-2 (10^{21} nvt, >500 ev, 540°F water) show that tensile strength was increased 20 to 30 percent in tests at room temperature, 570° and 750°F; yield strength was increased about 40 percent at room temperature and 750°F, and 45 to 55 percent at 570°F. Elongation was decreased by 50 percent. (24) The amount of hydrogen in the material (up to 250 ppm) did not affect the results. Data are shown in Table 6.

Table 7 presents a comparison of tensile data for irradiated Zircaloy-2 and -4. (14) The latter was irradiated for evaluation of its use in the CVTR. Note that the properties and effects of irradiation on stress are similar for both alloys.

Figures 39, 40 and 41 show the effect of irradiation on the room- and elevated-temperature properties of annealed and cold-worked Zircaloy-2. (2)

Figures 42 through 45 illustrate the effect of irradiation on Zircaloy-2 tensile properties as a function of increasing neutron dosage and post-irradiation test temperature. (4)

In a burst test of Zircaloy tubing for the NPD-II reactor irradiated to 2×10^{20} nvt (>0.5 Mev), the following results were observed: (24)

	<u>Unirradiated</u>	<u>Irradiated</u>	<u>Change, %</u>
Burst Strength, psi	63,000	73,000	+16
0.2% Yield Strength, psi	61,000	72,000	+18
Increase in Diameter, %	20	4.1	-20
Reduction in Area, %	26	21	- 5

THERMAL CONDUCTIVITY

ZIRCALOY

FIG. 38

TABLE 6

EFFECT OF NEUTRON IRRADIATION AND HYDROGEN CONCENTRATION ON
THE PROPERTIES OF ZIRCALLOY-2

(Each result is an average for three specimens)

TESTING TEMP.	HYDROGEN CONTENT ppm	0.2% PROOF STRESS		ULTIMATE TENSILE STRENGTH		ELONGATION	
		Unirradiated kgf/mm ²	Irradiated kgf/mm ²	Unirradiated kgf/mm ²	Irradiated kgf/mm ²	Unirradiated %	Irradiated %
Room Temp.	0	56.6	77.3	66.1	78.7	12.4	5.3
	20	62.0	85.8	70.0	85.8	18.5	6.8
	100	61.8	83.4	70.3	83.7	15.2	7.3
	250	60.5	84.4	70.7	84.4	14.1	6.2
300°C	0	29.7	45.0	33.5	45.0	12.8	5.8
	20	30.1	47.1	33.1	47.1	17.9	7.4
	100	29.7	45.7	33.60	45.7	21.8	8.5
	250	32.2	46.4	36.34	46.4	19.0	8.8
400°C	0	27.5	37.3	29.0	37.3	11.1	6.8
	20	26.5	37.3	28.1	37.3	8.7	10.5
	100	25.9	36.6	27.5	36.6	18.0	9.9
	250	27.2	36.6	28.4	36.6	17.4	10.7

TABLE 7

Effect of Irradiation on Tensile Properties of Zircaloy-2 and -4

Mat'l., Condition, Fast Exposure, nvt > 1 mev	Test Temp F	0.2% Y.S. (psi)	Ult. Str. (psi)	Uniform Elong. (%)	Total Elong. (%)	Red. of Area (%)
Zr-4, Annealed Unirradiated	Room	48,100	73,300	15.0	22.9	41.5
Zr-4, Annealed 1.0×10^{21}	Room	79,600	90,000	3.7	11.4	36.6
Zr-4, Annealed 1.4×10^{21}	Room	80,600	90,000	3.6	11.4	32.3
Zr-2, Annealed Unirradiated	Room	45,300	70,500	16.7	26.3	39.9
Zr-2, Annealed 1.0×10^{21}	Room	82,000	89,200	3.2	12.3	39.1
Zr-2, Annealed 1.4×10^{21}	Room	76,000	82,000	3.1	11.8	39.3
Zr-4, Annealed Unirradiated	300	35,100	56,500	13.0	23.9	42.1
Zr-4, Annealed 1.0×10^{21}	300	67,100	70,800	2.8	12.0	39.1
Zr-4, Annealed 1.4×10^{21}	300	69,000	72,200	2.2	11.6	39.9
Zr-4, Annealed 2.5×10^{21}	300	74,600	76,000	1.1	9.3	37.2
Zr-4, As Extruded, Unirradiated	300	53,800	73,700	9.3	21.4	50.5
Zr-4, As Extruded, 1.0×10^{21}	300	82,100	87,400	1.5	11.2	49.2
Zr-4, As Extruded, 1.4×10^{21}	300	85,800	88,000	0.6	9.4	49.7
Zr-4, As Extruded, 2.5×10^{21}	300	93,800	95,000	0.7	8.8	46.3
Zr-4, Hydrided, As Extruded Unirradiated	300	55,900	72,400	6.9	20.7	45.6
Zr-4, Hydrided, As Extruded 2.5×10^{21}	300	95,000	96,800			
Zr-4, Hydrided, Annealed, Unirradiated	300	34,900	54,300	11.2	24.6	40.3
Zr-4, Hydrided, Annealed, 2.5×10^{21}	300	71,600	74,800	1.5	10.0	39.1
Zr-4, Annealed Unirradiated	550	21,200	40,600	15.7	27.0	48.0
Zr-4, Annealed 1.0×10^{21}	550	49,200	49,200	0.6	13.7	50.9
Zr-4, Annealed 1.4×10^{21}	550	48,800	49,100	0.6	12.9	45.1
Zr-4, Annealed 2.5×10^{21}	550	59,000	59,000	0.2	10.0	42.2

FIG. 39

FIG. 40

FIG. 41

FIG. 42 - Effect of Fast-Neutron Exposure on the 0.2% Offset Yield Strength of Zircaloy-2.

FIG. 43 - Effect of Fast-Neutron Exposure on the Ultimate Tensile Strength of Zircaloy-2.

FIG. 44 - Effect of Fast-Neutron Exposure on the Total Elongation of Zircaloy-2.

FIG. 45 - Effect of Fast-Neutron Exposure on the Uniform Elongation of Zircaloy-4.

Impact Strength - Some observations of impact strength after irradiation to 10^{21} nvt (>500 ev) at 535°F are illustrated by the data in Figure 46.(24) Strength was decreased by the exposure to neutrons and by hydrogen in this study. Other investigations have reported no effect on impact properties.(4)

For annealed Zircaloy-4, impact properties of unirradiated specimens were found to be decreased slightly by hydriding to 100 ppm, however, post-irradiation toughness of similarly hydrided material was equal to or greater than the unirradiated values.(14) This phenomenon has also been observed by AECL for Zircaloy-2.(3) The impact properties of the hydrided Zircaloy-4 were unchanged by irradiation in the CVTR study.(14)

Modulus of Elasticity - Reportedly there is no significant effect on the modulus of elasticity for Zircaloy-2 after irradiation to 6×10^{21} nvt fast flux.(4)

Creep Resistance - Figure 47 shows the results of a continuous in-reactor test on the creep rate of Zircaloy-2.(24) Some conclusions drawn from this experiment are that little difference exists between in-reactor and ex-reactor primary and early secondary creep. Neutron flux increases the later secondary creep rate. In this experiment, the material has attained a steady-state secondary rate in contrast to ex-reactor rates which generally decrease.

Irradiation appears to have no effect on the short-time 100-hour creep properties of annealed or as-extruded Zircaloy-4 at 550°F and 20,000 psi.(14) A strain aging effect seems to be active in that nearly all the strain occurs during the first hour of testing.

Recovery - Figures 48 and 49 illustrate how irradiation (2.7×10^{20} nvt, fast) and post-irradiation annealing affects the recovery of tensile properties in annealed and cold-worked Zircaloy-2.(2) Figure 50 shows the relationship of temperature to recovery in unirradiated cold-worked material held at pile ambient temperature.(2) Recovery was found to be insignificant, irradiated or unirradiated, below an annealing temperature of about 535°F .

Corrosion and Hydriding Rates - The following summary (Table 8) of observations of the corrosion and hydriding of Zircaloy-2 illustrates the uncertainty in these respects which obtains at the present level of experience with Zircaloy in reactor environments.(46) A comprehensive summary of effects by other investigators is presented in Reference 47.

To summarize the mutual effects of irradiation, corrosion and hydriding on Zircaloy, Figures 51 and 52 show the changes in tensile and impact properties which occur in Zircaloy-2.(4)

FIG. 46 - Impact strength of cold-worked Zircaloy-2.

FIG. 47 - In-reactor creep tests of Zircaloy (16% cold work) at 300°C and 14 kgf/mm². Dashed curve shows results for a similar specimen not in the reactor.

FIG. 48

UNCLASSIFIED

FIG. 49

UNCLASSIFIED

FIG. 50

TABLE 8

OBSERVATIONS OF CORROSION AND HYDRIDING RATE IN REACTOR ENVIRONMENTS⁽⁴⁶⁾

<u>Reactor</u>	<u>Fast Flux, nvt</u>	<u>Temperature, OF</u>	<u>Environment</u>	<u>Velocity, fps</u>	<u>Corrosion Rate Change</u>	<u>Hydrogen Pickup Fraction</u>
ETR	7×10^{13}	550	Water	30	Increased by a factor of 30	10% increase
PWR	7×10^{14}	550	Water	10	No change	No change
Harwell	7×10^{11}	500-750	Steam	Low	No change	No change
Harwell	7×10^{12}	500-750	Steam	Low	Increased by a factor of 10 at 500°F	No change
Harwell	7×10^{13}	500-750	Steam	Low	No change at 750°F	No change
Dresden	7×10^{13}	550	Boiling Water	5	Increased by a factor of 15	< 10%
NPD-II	7×10^{13}	550	Water	27	Decreased	15%

FIG. 51 - Prediction of Hydrogen Pickup by Zircaloy-2 and Zircaloy-4 Plates in the Core of the N.S. SAVANNAH Reactor.

REF: CRMet-849, p 50, Fig.17

FIG. 52 - Effect of Hydrogen on Elongation of Zircaloy-2.

OTHER FACTORS CONCERNING THE MARK-V APPLICATION

Regulatory Body Approval for Reactor Materials and Construction

Normal legal commitments for the operation of a power reactor, such as the proposed 630A Maritime Nuclear Steam Generator, require adherence to ASME Boiler and Pressure Vessel Code allowances* for design stresses on materials and weldments used in the construction of pressure-containing vessels and other components. The pressure tubes of the Mark V-A and -B proposals are Class A structures as defined in Section III, Nuclear Vessels, of the Code. Zircaloy is not now an ASME Code-approved material, therefore a Code case petition must be prepared and approval received for use in the 630A application. Concurrent approval is also required of materials and construction for shipboard propulsion reactors under U.S. Coast Guard⁺ and American Bureau of Shipping^Δ regulations. Approval criteria for materials, designing and fabrication are similar and somewhat inter-related for the three sets of requirements. For example, CG-115 requires the use of ASME Code practices for design and preliminary approval of materials. CG-115, however, requires its own inspection to qualify welding practices.

Detailed requirements for a Code Case petition are presented in Reference 48. Table 9 summarizes typical mechanical property items for each of a number of heats or lots necessary to establish design stress allowances and weldability for Code Case approval. Data are to be obtained from as large a number of lots of material as practical to adequately define a normal range of property values. The bi-metal joint considered in the Mark V-A calandria tube design is a unique configuration and Code procedures for welded joint qualification do not apply. Code criteria for brazed joints will be used as a guide for evaluation.

Joining of Zircaloy to Dissimilar Metals

A number of approaches to the problems of Zircaloy-dissimilar metal bonding have been considered for reactor applications.⁽⁴⁹⁾ Welding has been unsuccessful due to the brittle intermetallic compounds formed in the joint. Brazed joints usually suffer from low strength, inferior corrosion resistance, or both. Brittle intermetallic also have rendered diffusion bonding unsatisfactory. Mechanical joints formed by rolling have been successful in some instances, such as CANDU and the N-Reactor, but a metallurgically bonded joint seems preferable in most cases.

*Section III, Nuclear Vessels, ASME Boiler and Pressure Vessel Code.

⁺CG-115, Marine Engine Requirements and Material Specifications.

^ΔRules for Building and Classifying of Steel Vessels, 1964, also Guide for Classification of Nuclear Ships, 1962.

TABLE 9

MECHANICAL PROPERTY DATA^a NEEDED FOR APPROVAL OF ZIRCALOY UNDER ASME BOILER
AND PRESSURE VESSEL CODE REQUIREMENTS

Zircaloy Base Metal		Zircaloy-Zircaloy Weldments		Zircaloy-Incoloy 800 Bi-Metal Joint	
Property	Range, °F	Property	Range, °F	Property	Range, °F
Ultimate Tensile Strength	RT-500	Reduced-Section Tensile	RT	Tensile Strength	RT-500
0.2% Yield Strength	RT-500	Guided Bend	RT		
Reduction of Area	RT-500	Compressive Strain	RT-500		
Creep Strength	400-500	Metallurgical Stability	RT-500		
Stress-Rupture	400-500	Retention of Properties	RT-500		
Strain Fatigue	400-500	Effect of Later Fabrication	RT-500		
Impact Strength	RT-500	Irradiation Effects	RT-500		
Elongation	RT-500				
Irradiation Effects	RT-500				

^aAll data are for material in the annealed condition. Code requirements do not permit cold-worked properties for design stress allowance. Base metal and weldments categories must be supplemented with information regarding accumulated service experience with the material. Other property tests, particularly of the joint, would be conducted to satisfy Company interest in the material's over-all suitability.

Several promising new techniques are presently under serious study. They include tandem extrusion, explosive forming and friction welding. The extrusion and explosion methods seem potentially useful for the 630A application.

Tandem Extrusion - The tandem extrusion process, developed principally by Nuclear Metals, Inc., (50) produces tubing having an overlapping tapered joint. The tube blank is a carefully machined, jacketed assembly. Extrusion requires about 50 tons at 14000 to 16000°F. Only one joint is produced from each extrusion. The tube must be finish-machined to remove the jacket material.

The ratio of joint length to tube thickness is about 50 to 1 for optimum properties. A feature of the process is that the inter-metallic layer is less than 0.001 inch thick. Nuclear Metals claims that 40 percent cold-work is possible with no damage to the joint. The tensile and shear strengths of the bond approach that of Zircaloy-2.

The tandem extruded joint has not seen extensive service in a true application, but many organizations have evaluated it. (51-53) Among these are GE-APED (Zircaloy-Incoloy 800), KAPL (Zircaloy-Inconel), Pratt and Whitney (Stainless Steel-CbZr), ORNL (Stainless Steel-Titanium), GNEC (Zircaloy-Inconel), HAPC, SRL and Bettis. Joints produced by this technique have three major disadvantages for 630A use: (1) the long overlap required, (2) the third joint required to form a full length calandria tube from two single extrusions, and (3) the high cost, \$400 to \$700 for 2 to 4 inch diameter tubing.

Explosive Forming - This process is undergoing development in the United States principally by Battelle Memorial Institute. (54,55) Zircaloy has been bonded to Inconel 600, and Types 304 and 410 stainless steel, but no joints produced by this method have seen any reactor pressure tube service. A cooperative USAEC/AECL program was at one time implemented to produce bi-metal tubing for the NPD-II and CANDU reactors. The study was precluded by the development of suitable mechanical roll-bonding techniques at Canadian General Electric.

In the explosive process, the tubes to be joined are machined to form an initial overlap. Zircaloy would be the outer tube at the joint. An explosive charge contained in a parawax block is placed inside the assembled tubes within the area to be joined. A heavy back-up ring is usually positioned around the outside of the joint area. The explosive charge is detonated and the high energy shock wave forces the tubes together forming a metallurgical bond. No fusion zone intermetallic compound formation is detectable in the joint.

Transition joints may be formed at both ends of a single Zircaloy tube for the 630A calandria application. The joints need only be a few inches long to develop shear strength equivalent to or better than the strength of the weaker material. The method is less expensive than tandem extrusion, but is limited to about 1/8-inch wall thickness.

Procurement of Zircaloy-2 and -4

A summary report on the procurement of tubing for the Hanford N-Reactor describes some of the industrial capability and economic factors involved.⁽¹⁷⁾ Very little was known about Zircaloy-2 tube fabrication as recently as 1957. Equipment at that time was limited and technology was virtually non-existent for producing 60-foot long, 3-1/4-inch diameter, 1/4-inch wall, high tolerance tubes. Zircaloy-2 as 1000-pound ingots cost \$14 to \$15 per pound at that time. Currently it costs about \$2.40 per inch as 3-1/2 inch OD by 0.020 inch wall tubing.⁽⁴⁹⁾ In the space of three years, the procurement of Zr products progressed from a questionable market and marginal technology to competitive bidding and quality stated to be better than standard steel tubing. Hanford procured 1064 tubes with 97 percent acceptance based on the inspection program contained in Reference 17.

Some U.S. Bureau of Mines information on Zr alloy ingot and quality of Zircaloy-4 is presented in Table 10.⁽¹⁴⁾

TABLE 10

ZIRCONIUM ALLOY PRODUCTION

<u>Year</u>	<u>Zr Alloy Ingots, pounds</u>	<u>Estimated Percent of Production for Zircaloy-4</u>
1960	2,690,000	Very small
1961	3,449,000	10
1962 (April)	468,000	15-20

Some of the companies which have a capability for producing Zircaloy ingots and tubing are:⁽²⁵⁾

The Carborundum Company	Ingot
Wah Chang Corporation	Ingot
ICI	Ingot
Harvey Aluminum Company	Ingot, Tubing
Chase Brass & Copper Company	Tubing
Allegheny Ludlum	Tubing
Tube Reducing Company	Tubing

Alloys of Zr Containing Nb

The exploitation of Zr for reactor service has spawned many alloy development programs beyond the Zircaloy series.(5,57-59) The aims are, of course, higher temperature capability for economy in power reactors. One such alloy appearing to hold some promise is the Zr-2.5Nb composition. It has higher strength than Zircaloy-2 (90,000 versus 70,000 psi), but corrosion resistance is variable and only about equal to Zircaloy corrosion resistance. For the present 630A applications, the properties of Zircaloy are adequate, although further development of the Zr-Nb system or others will be followed.

CONCLUSIONS

1. Both Zircaloy-2 and -4 possess adequate strength and corrosion resistance for use in the proposed 630A Mark-V reactor designs.
2. The properties of Zircaloy-2 and -4 are essentially equivalent.
3. Neither alloy appears seriously affected by irradiation to 2×10^{21} nvt, fast flux.
4. Quantities of hydrogen greater than that estimated to be absorbed during 630A exposure do not cause significant property changes in either alloy.
5. Available mechanical property data and service experience for Zircaloy-2 may be sufficient to prepare a suitable Code Case petition.
6. Explosive forming is a potentially useful technique to joining Zircaloy to a dissimilar metal, such as Incoloy 800, for the calandria-type design.
7. The propensity of Zircaloy-4 to absorb less hydrogen than does Zircaloy-2 is its principal advantage.

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