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GEAP-10044
JOINT U.S.-EURATOM RESEARCH
AND DEVELOPMENT REPORT
JUNE 1969

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**SPECIFIC ZIRCONIUM ALLOY
DESIGN PROGRAM
FINAL SUMMARY REPORT**

H.H. KLEPPER
A.S. MEHNER

U.S. ATOMIC ENERGY COMMISSION
CONTRACT AT(04-3)-189
PROJECT AGREEMENT 24

NUCLEAR FUELS DEPARTMENT

GENERAL ELECTRIC

SAN JOSE, CALIFORNIA

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EURAEC
GEAP-10044
Joint U. S.-Euratom Research
and Development Report
June 1969

**SPECIFIC ZIRCONIUM ALLOY DESIGN PROGRAM
FINAL SUMMARY REPORT**

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Prepared for the
U. S. Atomic Energy Commission
Contract AT(04-3) 189
Project Agreement 24
for the
Joint U. S.-Euratom Research and Development Program

NUCLEAR FUELS DEPARTMENT
GENERAL ELECTRIC
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5926-NFD-121
145-AG-10/69

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FOREWORD

The United States and the European Atomic Energy Community (EURATOM) on May 29, and June 18, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of the peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a joint U.S.-EURATOM research and development program which is aimed at reactors to be constructed in Europe under the joint program.

The work described in this report represents the Joint U.S.-EURATOM effort which is in keeping with the spirit of cooperation in contributing to the common good by the sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in Western Europe and the United States.

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The discussions and data given by Al Reisen of Wah Chang Corporation regarding the melting and hot-working operations, Jack Huber of Wolverine Tube on warm extrusion operations, and Ed Baroch and Don Honens of Wah Chang Corporation for straightening the finished tubes, were most appreciated.

The irradiation tests in the Big Rock Power Station and the fuel pool examinations there could not have been accomplished without the administrative and technical support of many of the personnel of Consumers Light and Power Company, particularly Robert Hauter, Cy Hartman, Robert Biggs, and Dave Bixell.

ABSTRACT

The termination of the joint U.S.-Euratom research and development agreement on June 30, 1969, simultaneously brings to a close joint sponsorship of the Specific Zirconium Alloy Design Program. The objective of the program was to develop a Zr-Cr alloy as a functional cladding. The Final Summary Report is a compilation of the data accumulated on the mechanical and physical properties of the Zr-Cr alloy, and the detailed results of the irradiation program up to June 30, 1969.

Under the Specific Zirconium Alloy Design Program, a Zr + 2.0 at.% Cr + 0.16 at.% Fe alloy (Zr-Cr) with superior high temperature corrosion resistance has been developed. A commercially feasible process has also been developed and successfully used to fabricate significant quantities of tubing and bar stock from large ingots of the alloy. Characterization tests confirmed this process to result in tubing with excellent high-temperature (up to 500°C) steam autoclave corrosion resistance. The mechanical properties of the tubing were equivalent to present Zircaloy-2 fuel cladding.

Zr-Cr alloy clad fuel rods have been successfully irradiated in the Consumers Big Rock Point reactor to an average exposure of 14,300 MWd/tU. The Zr-Cr clad fuel rods have performed as well as, and often better than, Zircaloy-2 clad fuel rods under similar irradiation conditions. During the last BRP irradiation cycle, the Zr-Cr cladding received a stringent test of its primary performance advantage, i.e., improved corrosion resistance at overtemperature conditions. Crud deposition during the cycle was abnormally high, leading to cladding surface temperatures significantly beyond design limits. Under these conditions, one Zr-2 rod in the bundle failed, while all Zr-Cr rods remained intact.

A detailed post-irradiation examination to evaluate the corrosion behavior of the Zr-Cr alloy as fuel cladding has been performed on nine fuel rods (six Zr-Cr clad rods and three Zr-2 clad rods) irradiated to an average exposure of 8000 MWd/tU (7900 hours), and two dummy rods exposed for 7900 hours. For these exposures, the Zr-Cr alloy performed satisfactorily as a fuel rod cladding. Oxide film thickness measurements taken on the Zr-Cr fuel cladding and the Zircaloy-2 fuel cladding indicate the Zr-Cr alloy's corrosion behavior in-pile at these exposures is as good as or better than the corrosion behavior of Zircaloy-2.

Long-term, out-of-pile, loop corrosion tests have been performed on the Zr-Cr alloy and Zircaloy-2. The corrosion loop simulates the environments (including heat transfer) fuel rods would be exposed to in a boiling water environment. The results of these corrosion tests after 7800 hours exposure have been compared directly with the in-pile corrosion results, and the effects of heat transfer, irradiation, and surface pretreatment on the corrosion rates of the Zr-Cr alloy have been evaluated. Up to 7800 hours exposure, heat transfer conditions have no effect on the corrosion rate of the Zr-Cr alloy. Irradiation enhances the corrosion rate of both the Zr-Cr alloy and the Zr-2 alloy. The effect of surface pretreatment on the corrosion rates of the Zr-Cr and Zr-2 alloys is not clear; however, there are indications that the corrosion increases with higher temperature autoclave prefilms.

1. INTRODUCTION

This is the Final Report summarizing work performed on the Specific Zirconium Alloy Design Program.* This program was initiated on January 29, 1962, as a 2-year program, and was reactivated in November 1964 for the evaluation of a Zr + 2 at.% Cr + 0.16 at.% Fe alloy as cladding for water reactor fuel. The program is being terminated now with the expiration of the USAEC-Euratom Joint Research and Development Program.

The original 2-year program, which developed the alloy composition of interest for the subsequent fuel cladding tests, was summarized on April 15, 1964, in a report entitled "Specific Zirconium Alloy Design Program -- Summary Report" (GEAP-4504, EURAEC-1193) (Ref. 1). This Final Report will emphasize the development of a process for making fuel cladding tubes of the alloy, the properties of the tubes fabricated, and the in-pile behavior of fuel clad with the alloy tubes. Further details on the program can be obtained from the reports listed in Appendix A (a list of all of the reports issued during the course of the program since its inception in 1964).

In the original alloy investigations, a Zr + 2.0 at.% Cr + 0.16 at.% Fe alloy (which will hereafter be designated "Zr-Cr

alloy") was developed with the potential for improved service reliability as water reactor fuel cladding (Ref. 2). Of the 31 zirconium alloys tested in the original program, including Zircaloy-2, this composition was shown to have far better corrosion resistance at temperatures above 300°C (see Figure 1-1); for the best heats, no transition or "breakaway" in corrosion kinetics was observed in over 8000 hours for the Zr-Cr alloy, even at 500°C. An important characteristic was the alloy's lower increase in corrosion rate with increasing temperature (see Figure 1-2). It was felt that the alloy might offer protection in reactor service against overtemperature conditions (which could otherwise result in excessive corrosion of the present water reactor cladding alloys, Zircaloy-2 and Zircaloy-4). Although this superior high-temperature water corrosion resistance was demonstrated in the laboratory (and has since been confirmed in a number of other laboratories), there was at that time (and is even now) no direct way to predict in-reactor performance of any zirconium alloy. Therefore, irradiations of the alloy as actual fuel cladding were performed. The requirement to test the alloy as fuel cladding also implied the development of a practical method for processing the alloy to tubing (and to bar stock for end plugs).

2. DEVELOPMENT OF TUBING FABRICATION PROCESS

2.1 VARIABLE PERFORMANCE FIRST VENDOR TUBING

To evaluate the Zr-Cr alloy as water reactor fuel cladding, it was first necessary to demonstrate that tubing could be fabricated from the alloy in a practical way under full-scale conditions. The first tubing material was processed (Figure 2-1) side by side with a companion Zircaloy-2 ingot by commercial zirconium vendors. No differences in ease of processing between the two alloys were observed. The final tubing met all normal ASTM chemical, dimensional, surface finish, grain size, and corrosion specifications (Ref. 3). Before committing the tubing to fuel irradiation, however, a more detailed evaluation was performed to determine whether the potential of the alloy composition revealed in laboratory tests was actually realized on vendor material.

Evaluation of the corrosion resistance of this first batch of tubing at several temperatures in three different corrosion test facilities revealed variable corrosion performance after long times (500 to 1500 hours). The nature of the variable corrosion behavior of the first vendor material is delineated

by the appearance of the sample shown in Figure 2-2. Some samples (i.e., some surface regions of the samples shown in Figure 2-2) exhibited black oxide films and low weight gains; others exhibited inhomogeneous, white oxide films and high weight gains. Laboratory-fabricated coupons run side by side with the vendor material in the same tests consistently confirmed the potential of the alloy composition for excellent corrosion resistance and, by comparison, accentuated the variable behavior of the tubing.

Several possible explanations for the difference in behavior between laboratory material and vendor-produced material were explored and rejected by investigative evidence:

- Sample preparation or test conditions*—rejected because laboratory and vendor material run side by side performed differently (Ref. 4).
- Surface nitrogen contamination*—rejected by multiple chemical analyses which revealed no surface contamination and a bulk concentration equivalent to that for good laboratory melts (Ref. 4).

*USAEC Contract AT(04-3)-189, Project Agreement No. 24.

Figure 1-1 Steam Corrosion Data - - 300°C, 400°C, and 500°C Exposure

Figure 1-2 Corrosion Rate of the Zr-Cr Alloy as a Function of Temperature

(1) FIRST NUMBER IS OUTSIDE DIAMETER OF TUBE, SECOND NUMBER IS WALL THICKNESS.

Figure 2-1 Flow Diagram of Process Used in Fabrication of First-Round Commercial Zr-Cr Tubing

- c. *Chemical composition*—rejected by comparison of vendor and laboratory sample chemical analyses (Ref. 4).

In performing these tests, however, useful information on proper etching and cleaning of the Zr-Cr alloy was obtained, and the tolerance of the alloy for nitrogen contamination was experimentally determined. These results are summarized in Appendixes B and C, respectively.

The difference between the vendor material and the laboratory material was found to be related to the size and distribution of the intermetallic particles in the alloy, and thus to differences in process history (temperatures, times-at-temperature, and cooling rates). A full-scale, 555-kg ingot was processed by the vendor; 1.8-kg ingots were melted in the laboratory. At each point in the processing, the larger sections of the vendor material cooled more slowly. From the thermal properties of zirconium and the known dimensions and cooling media, the cooling rates can be estimated:

Process Step	Calculated Cooling Rates (°C/sec)	
	Vendor	Laboratory
Ingot	0.8	22
Forging	0.6	2.5
Solution Quench, bar	7	
Solution Quench, tubing	11 to 28	67 to 90

It was also thought possible that the vendor forging of the Zr-Cr material included processing at temperatures in the two-phase, alpha-plus-beta region; this region was avoided for Zircaloy-2. The temperature limits for the two-phase region were estimated to be lower for Zr-Cr than for Zircaloy-2 since the tin in Zircaloy-2 is an alpha stabilizer.

Times at temperature also differed. Data were taken during laboratory processing; the process times for vendor material were estimated (from discussion with the vendor) as follows:

Figure 2-2 Inhomogeneous Oxide Film Breakdown on Zr-Cr Bar Exposed to Refreshed Steam at 500°C

Process Step	Vendor	Estimated Time (minutes)	Laboratory
Forging	840 (1/3 in $\alpha + \beta$)		180
Solution-treatment	180-300		120-360
Hot-Working	240 (extrude)		200 (roll)
Intermediate Cold-Working anneals	780 (five anneals)		120 (one anneal)

The big differences were in forging times and in the time for intermediate cold-working anneals. (For some laboratory melts, annealing times of 480 minutes were used, but only at 565°C; the comparison shown is for 760°C where the tubing was processed.)

Such differences in process history should be reflected in differences in microstructure. The slower cooling vendor ingots, processed for longer times, might be expected to show more coarse intermetallic precipitates. A comparison of the tubing microstructure with that for the best laboratory melt, 201C*, shown in Figure 2-3, demonstrates that this was true. The microstructure of the tubing viewed at lower magnification further revealed a banded inhomogeneous distribution of the intermetallics (Figure 2-4). This banding was believed to be related to segregation of the chromium to the beta phase during processing the two-phase region. Evidence for this segregation is given in Figure 2-5 which shows the microstructure of an unprocessed tubing extrusion billet. The size and distribution of the intermetallics in sheet fabricated from the vendor forging and annealed at 788°C are shown in Figure 2-6.

The possible correlations between microstructure, process history, and corrosion performance were:

- Slower cooling rates promoted poor corrosion performance. The quenching rate for the tubing extrusion billets was perhaps a little slower than the laboratory ingot cooling rate.
- The more inhomogeneous distribution of the intermetallics as a result of processing in the two-phase region led to inhomogeneous film breakdown (see Figure 2-2 showing a Zr-Cr bar sample exposed at 500°C) and variable corrosion performance among samples in the same test. The uniform distribution of intermetallics for the laboratory material correlated with reproducible corrosion performance.
- Long annealing times, high in the alpha temperature range, produced coarse intermetallics and poorer corrosion performance.

*Zr + 2.3 at.% Cr + 0.05 at.% Fe processed entirely at 788°C.

If the difference in corrosion performance between the laboratory melts and the vendor material were related to differences in intermetallic size and distribution which, in turn, were controlled by process history, then it should have been possible to reverse the relative corrosion performance of laboratory and vendor material by reprocessing. To test this corollary, a piece of the worst vendor material, the unquenched forging, was remelted and fabricated to sheet in the same way as laboratory material. Samples of three good laboratory-fabricated batches were resolution-treated, but slow-cooled through the two-phase region. Both materials were exposed to refreshed steam at 500°C and to static steam at 400°C. As the data in Table 2-1 show, the remelted vendor material did perform better than the slow-cooled laboratory samples — confirming the general diagnosis of the cause of the poor performance of the first batch of vendor tubing.

2.2 PHYSICAL METALLURGY STUDIES — FABRICATION AND CORROSION

Although it was demonstrated that the Zr-Cr alloy could be fabricated in a practical way to meet ASTM specifications for fuel cladding tubes, variable corrosion behavior associated with coarse intermetallic particles demanded modification of the first fabrication procedure. Physical metallurgy and corrosion studies were first performed to determine the fabrication step (or steps) leading to intermetallic particle coarsening, and to determine the proper corrective changes in the fabrication procedure. These studies led beyond the role of precipitate particles per se to a deeper understanding of the relationship between heat treatment, microstructure, composition, and corrosion behavior.

2.2.1 TRANSFORMATION TEMPERATURES — THE ALPHA-PLUS-BETA REGION

The two-phase temperature boundaries were determined by dilatometry with a Leitz Model UBD vacuum dilatometer. The samples were rods 4 cm long by 0.33 cm in diameter. Graphite flake was used to separate the alloy samples from the quartz sample holders to prevent reaction and sticking.

750X

a Laboratory Melt 201C

750X

b 1.14-cm-diam Rocked Tubing

Figure 2-3 Size and Distribution of Intermetallics

100X

Figure 2-4 Banding of Intermetallics in 1.14-cm-diameter Ricked Tubing

250X

Figure 2-5 Zr-Cr Extrusion Billet Microstructure

750X

Figure 2-6 Microstructure of Sheet Fabricated from Vendor Forging. Final Anneal 8 Hours at 788°C

TABLE 2-1
Comparison Between Refabricated Vendor Zr-Cr Alloy
And Slow Cooled Laboratory Metal Zr-Cr Alloy

500°C – Refreshed Loop – Steam – 1000 psi

Sample Designation	Condition	Weight Gains (mg/dm ²)	
		168 h	456 h
V-1	Vendor forging	65.2	105.8
V-2	Refabricated	61.7	99.5
V-3	With rapid cooling	63.0	103.3
223-1	Laboratory material	93.6	207.0
622-1	Slow-cooled	86.5	185.7
722-1		94.2	196.3
722-2		81.6	174.2

400°C – Static Autoclave – Steam – 1500 psi

V-4	Vendor forging	16.3	22.6
V-5	Refabricated	15.2	20.3
V-6	With rapid cooling	15.5	20.6
223-2	Laboratory material	15.0	24.0
622-2	Slow-cooled	18.5	26.7
722-3		16.0	24.0

Seven samples were tested. One sample was machined from an extrusion billet, two were machined from bar stock produced with the first vendor material (Ref. 4,5) and four more samples were machined from a sponge-base laboratory melt of Zr-Cr (see Table 2-2 for chemical analysis). The most satisfactory runs were those in which beta solution-treated (955°C, 1 hour) and quenched samples were used. The results of one such run are shown in Figure 2-7; the heating rate was 16.7°C/h and the cooling rate 9.4°C/h, at temperatures between 700 and 1000°C.

TABLE 2-2
ANALYSIS OF Zr-Cr ALLOY MATERIAL

<i>Alloy Additions (wt%)</i>			
Cr*	1.11 ± 0.04		
Fe*	0.09 ± 0.02		
<i>Impurity Level (ppm)</i>			
N*	14	Mn	<20
Al	20	Ni	<35
B	< 0.2	Pb	<20
C	<80	Si	<30
Cd	< 0.2	Ti	<20
Co	<10	U	< 1
Cu	<20	W	<50
Hf	105		

* Analyses taken on final product. All other values are for the zirconium starting material.

On the basis of the results of the dilatometry runs, the temperature boundaries for the alloy two-phase region are 800 and 900°C. (Similar runs on Zircaloy-2 gave 850 to 950°C for the two-phase region.)

Thus, in fabricating the Zr-Cr alloy, with analogy to Zircaloy-2, holding in the alpha-plus-beta temperature range 800 to 900°C should be avoided.

2.2.2 PRECIPITATE COARSENING

An ingot (1.8 kg) of Zr-Cr was double-arc-melted under argon, forged at 955°C, solution treated 1 hour at 955°C, and quenched in water. The analysis for the material is that given in Table 2-2. Small cubes, approximately 1 cm on edge, were cut from the quenched forging. The cubes were sealed in Vycor under vacuum and annealed for various times at various temperatures. One set was cut from

material solution-treated for 75 minutes at 1050°C, warm-rolled 50% at 480°C, cold-rolled 30% before sealing in Vycor, and vacuum-annealed for 1, 10, and 100 hours at 540*, 605*, 675, and 760°C.** Typical metallographic results are shown in Figure 2-8 for the 760°C series.

Other samples (955°C solution-treated) were held 24 hours at 807, 837, 877, and 907°C (in and near the two-phase region). Figures 2-9 and 2-10 illustrate the metallographic results for this series.

Some additional samples from another study had been annealed 2 hours at 760, 780, or 820°C. Metallographic preparation involved normal grinding and polishing. Before etching, each sample was attack-polished on a slow-speed wheel with a slurry of Linde "B" Alumina Abrasive in an aqueous solution of 0.005% HF. An etchant composed of 60 ml glycerol, 25 ml nitric acid, and 5 ml HF was used as a final immersion etch for 20 seconds. This procedure was designed to highlight the size and distribution of inter-metallic particles.

Shown in Figure 2-11 is a summary of all the data on precipitate coarsening. The first batch of vendor tubing had many second-phase particles as large as 4 to 5.5 μ in diameter, and showed associated inhomogeneous film breakdown and variable corrosion performance. Of the reproducibly good laboratory samples, some had shown a few large particles at 2.5 μ . For the best laboratory samples, the largest particles were 1 μ , with the bulk of the precipitates less than 0.2 μ . Figure 2-11 shows the largest particles observed after annealing for various times of practical interest as a function of annealing temperature.

The data presented in Figure 2-11 provides a guide for minimizing detrimental precipitate coarsening during fabrication. Above 900°C, in the beta region, all inter-metallics are soluble. The sample annealed 24 hours at 907°C showed that the trend of increasing precipitate size with increasing temperature does not extend into the beta region.

Some of these same samples used for the metallographic studies were corrosion tested in 500°C, 1000 psi, refreshed oxygenated steam.* The results are presented in Table 2-3.

Figure 2-12 shows that long-term weight gain depends on particle size. Precipitate particle growth in the two-phase region (800 to 900°C) is clearly detrimental to corrosion resistance. For alpha-phase aging, a particle size between

* The corrosion test facilities used for all of the high-pressure, refreshed, oxygenated steam tests referred to throughout this Final Report are described in Appendix D.

** Duplicated runs with 955°C solution-treated material.

Figure 2-7 Dilatometry Run -- Zr + 2.0 at.% Cr + 0.16 at.% Fe

(a) 1 hour

(b) 10 hours

(c) 100 hours

Figure 2-8 Microstructure of Zr + 2.0 at.% CR + 0.16 at.% Fe After Annealing at 760°C (750X)

(a) 807°C

(b) 837°C

(c) 857°C

Figure 2-9 Microstructure of Zr + 2.0 at.% Cr + 0.16 at.% Fe After 24 Hours (750X)

(a) 877 °C

(b) 907 °C

Figure 2-10 Microstructure of Zr + 2.0 at.% Cr + 0.16 at.% Fe After 24 Hours (750X)

Figure 2-11 Precipitate Coarsening as a Function of Processing Temperature and Time at Temperature

Figure 2-12 Corrosion Weight Gain as a Function of Intermetallic Particle Size

TABLE 2-3
CORROSION WEIGHT GAIN AS A FUNCTION OF PARTICLE SIZE

ALPHA-PHASE PRECIPITATE COARSENING
(Laboratory melt, solution treated 1 h, 955°C,
water quenched, and aged as shown)

Temperature (°C)	Aging Treatment Time (hours)	Particle Size (μ)	500°C Corrosion Weight Gain (mg/dm ²)	
			291 Hours	1882 Hours
540	1	<0.3	137	594
	10	0.5	104	441
	100	0.9	92	488
605	1	0.3	129	574
	10	0.5	79	337
	100	1.1	83	308
760	1	0.4	78	211
	10	0.7	66	162
	100	1.7	90	230

TWO-PHASE PRECIPITATE COARSENING
(Laboratory melt, solution treated 1 h, 955°C,
water quenched, aged 24 hours, and water quenched)

Aging Temperature (°C)	Particle Size (μ)	500°C Corrosion Weight Gain (mg/dm ²)	
		291 Hours	1882 Hours
807	1.6	96	221
837	2.0	110	268
857	2.7	149	359
877	5.3	179	493
907	5.3	180	907

0.5 and 1.5 μ is desirable; however, aging the quenched structure first improves the corrosion resistance, but then as the particles coarsen, corrosion resistance diminishes. The weight gain is also dependent on aging temperature for a given particle size. Therefore the dependence of corrosion resistance on aging temperature below 800°C involves factors other than particle size alone.

Weight gain data from Table 2-3 have been plotted as a function of final aging temperature in Figure 2-13. From this plot, for these particular samples, it was concluded that optimum corrosion resistance results from alpha-phase aging at about 700 to 800°C.

2.2.3 PRECIPITATE DISSOLUTION ABOVE 900°C

Samples of the as-forged vendor Zr-Cr material (first tubing batch) were used to study solution kinetics above 900°C

because this material was known to contain large second-phase particles. Small cubes about 1 cm on edge were cut and sealed in Vycor capsules under vacuum. Different capsules were solution-treated for 20 minutes, 75 minutes, and 6 hours, at 955, 1000, or 1050°C. At the end of the appropriate time, the capsules were rapidly removed from the furnace, broken under water, and their contents were quenched. Metallographic preparation was the same as that for the precipitate coarsening samples.

The resultant microstructures for the 955°C series are shown in Figure 2-14. The precipitates were completely homogenized after 6 hours at 1050°C, as demonstrated by the microstructure (Figure 2-15). Local inhomogeneities in the microstructures persisted for 75 minutes at 1050°C and for 6 hours at 1000°C. Reduction of 7 μ diameter particles to less than 1 μ (a value consistent with good corrosion performance) was achieved in less than 2 hours at 955°C

Figure 2-13 Corrosion Weight Gain as a Function of Metallurgical History

(a) 20 minutes

(b) 75 minutes

(c) 480 minutes

Figure 2-14 Microstructure of Vendor Zr-Cr after Various Times at 955°C, Water Quenched (750X)

(Figure 2-16). Laboratory melt samples solution-treated for 1 hour at 955°C were observed to contain particles no larger than 2.5 μ ; This observation is consistent with the curve in Figure 2-16.

Companion precipitate solution samples were also corrosion-tested at 500°C in steam; the results are given in Table 2-4.

TABLE 2-4
CORROSION WEIGHT GAIN AS A FUNCTION OF METALLURGICAL HISTORY

PRECIPITATE SOLUTION EXPERIMENT

*(First batch vendor forging; all samples tested
as quenched from solution temperature)*

Solution Treatment Temperature (°C)	Time (min)	500°C Corrosion Weight Gain (mg/dm ²)	
		291 Hours	1882 Hours
955	20	213	692
	75	201	679
	480	201	689
1000	20	216	727
	75	200	972
	480	250	1030
1050	20	262	790
	75	229	778
	480	278	891

Figure 2-15 Microstructure of Vendor Zr-Cr after 480 minutes at 1050°C, Water Quenched (750X)

Figure 2-16 Precipitate Dissolution as a Function of Time at 955°C

Note that the weight gains for these samples, as-quenched after solution treatment above 900°C, are high relative to alpha-phase-aged samples (the weight gains are almost as high as those expected for the best Zircaloy-2 in this corrosion test). Thus, solution of the particles per se, putting all of the chromium (and iron) into solution, does not promote optimum corrosion resistance.*

2.2.4 CHROMIUM CONTENT IN SOLUTION

Since alpha-phase aging was found to be dependent not only on particle size, other factors were explored by comparing, in corrosion tests at 400 and 500°C, quenched versus aged samples of alloys of differing Cr content.

Small, sponge-base zirconium, non-consumably-melted buttons containing various chromium contents were prepared and hot-rolled to sheet. Half of each sheet was beta-solution treated at 955°C, water-quenched, and corrosion tested; the other half of each quenched sheet was

also given an aging treatment at 760°C for 2 hours before testing. Corrosion coupons were prepared by the procedure given in Appendix B. Tests were performed at 400 and 500°C in 1000-psi, refreshed, oxygenated (25 ppm O₂ + 3 ppm H₂) steam. Results from the 500°C test are presented as Table 2-5.

From analysis of the 500°C data, it is concluded that there is an optimum chromium content in solution at about 0.7 at.% Cr. Aging the quenched 2.0 at.% alloy 2 hours at 760°C reduces the chromium content in solution to about 1.0 at.%. This same analysis also leads to the conclusion that even with equivalent Cr content in solution, the quenched samples corrode faster.

The 400°C corrosion test results, Table 2-6, further show that chromium content in solution alone is not the single determining factor for corrosion rate. Aging is beneficial to all chromium contents.

* The corrosion performance of quenched material is also pertinent to the corrosion performance of fuel element welds. The results obtained here suggest that quenched Zr-Cr weld metal will corrode faster than the cladding but perhaps no faster than does Zircaloy-2. Fortunately, welds are not subjected to surface temperatures as high as those at the heat transfer cladding surfaces.

TABLE 2-5
EFFECT OF CHROMIUM CONTENT AND AGING
TREATMENT ON WEIGHT GAINS IN 500°C STEAM

Chromium Content (at.%)*		Average** Weight Gain (mg/cm) After				
Analysis	Treatment	98 Hours	656 Hours	1641 Hours	1854 Hours	1950 Hours
0.002	Quenched	6080	Spalling			
	Aged	6300	Spalling			
0.100	Quenched	4610	Spalling			
	Aged	5920	Spalling			
0.256	Quenched	815	Spalling			
	Aged	4700	Spalling			
0.503	Quenched	72	120	236	291	299
	Aged	703	Spalling			
0.753	Quenched	61	114	294	369	378
	Aged	224	Spalling			
1.03	Quenched	47	102	283	360	373
	Aged	64	114	182	223	229
1.63	Quenched	56	190	416	503	517
	Aged	50	101	166	215	222
2.04	Quenched	48	207	546	683	704
	Aged	45	107	222	290	302

* Iron Content 0.14 at.%.

** Two Coupons each value; standard deviation about $\pm 3\%$ of each value.

TABLE 2-6
EFFECT OF CHROMIUM CONTENT AND
AGING TREATMENT ON WEIGHT GAIN IN 400°C STEAM

Chromium Content (at.%) [*] Analysis	Treatment	Average ^{**} Weight Gain (mg/cm) After					
		98 Hours	656 Hours	1830 Hours	2190 Hours	2355 Hours	2475 Hours
0.002	Quenched	306	Spalling	Spalling	Spalling	Spalling	Spalling
	Aged	26	71	154	Spalling	Spalling	Spalling
0.100	Quenched	78	400	Spalling	Spalling	Spalling	Spalling
	Aged	22	68	58	Spalling	Spalling	Spalling
0.256	Quenched	69	241	Spalling	Spalling	Spalling	Spalling
	Aged	15	62	220	Spalling	Spalling	Spalling
0.503	Quenched	68	362	Spalling	Spalling	Spalling	Spalling
	Aged	16	65	273	Spalling	Spalling	Spalling
0.753	Quenched	62	215	Spalling	Spalling	Spalling	Spalling
	Aged	11	49	200	Spalling	Spalling	Spalling
1.03	Quenched	33	82	221	Spalling	Spalling	Spalling
	Aged	11	33	105	Spalling	Spalling	Spalling
1.63	Quenched	43	61	(128)	67	86	89
	Aged	13	31	62	52	60	63
2.04	Quenched	13	23	Not meas.	46	66	68
	Aged	13	26	Not meas.	43	49	50

* Iron content 0.14 at.%.
 ** Two coupons; standard deviation very high, about $\pm 25\%$.

Chromium contents left in solution after aging were deduced from the 500°C data. Lattice parameter measurements were attempted to confirm these values. The shift in x-ray peak positions did show the a_0 parameter decreasing and the c_0 increasing in the expected way as chromium content increased, but because of marked preferred orientation in the sheet specimens, precise lattice parameters could not be determined. The x-ray line-broadening data shown in Table 2-7 suggest that lattice strain in the quenched samples contributes to higher corrosion rates. The data show a trend to somewhat higher strains at higher chromium content. Aging reduces lattice strain in all cases.

Since the chromium content and the lattice strain are the same in the 760°C aged samples in both 400 and 500°C

tests, it is not surprising to see the same general behavior in both corrosion tests. The conclusion that the reduction in chromium in solution for the 2.0 at.% Cr alloy during aging is beneficial at both test temperatures seems valid. For quenched samples, the relaxation of lattice strain would certainly be faster in the 500°C test than in the 400°C test, with lattice strain effects masking the composition minimum effect seen at 500°C.

Clearly, for optimum corrosion performance at both temperatures for the Zr-Cr alloy, it is necessary to age to reduce lattice strain, but not to over-age so that chromium in solution is reduced below about 0.7 at.% Cr.

TABLE 2-7
THE EFFECT OF CHROMIUM CONTENT AND AGING TREATMENT
ON MATRIX X-RAY DIFFRACTION LINE-BROADENING

Chromium Content (at.%) Analysis	Treatment	X-Ray Line Breadth at 1/2 Peak Height	
		(100) Peak	(002) Peak
0.002	Quenched	10.7	11.6
	Aged	9.3	9.3
0.100	Quenched	10.8	14.3
	Aged	9.3	-
0.256	Quenched	10.4	13.4
	Aged	9.6	10.5
0.503	Quenched	11.1	-
	Aged	9.5	-
0.753	Quenched	12.4	12.6
	Aged	10.5	-
1.03	Quenched	11.4	15.2
	Aged	10.1	9.5
1.63	Quenched	16.0	16.0
	Aged	10.2	9.8
2.04	Quenched	13.0	-
	Aged	10.0	11.0

2.2.5 DISCUSSION

The objective of these physical metallurgy studies on fabrication and corrosion was to determine the fabrication step(s) leading to intermetallic particle coarsening, and to determine proper corrective changes in the fabrication procedure. It had been postulated that the variable performance of the first batch of vendor-produced tubing was related to the inhomogeneous distribution of large intermetallic particles in this material. It was further postulated that the nonuniform distribution was caused by segregation of chromium to the beta phase during fabrication in the two-phase temperature range. Neither segregation nor coarse particles were observed for laboratory samples which showed consistently good corrosion performance.

With one exception, no laboratory material had been fabricated between 800 to 900°C. The exception was some samples forged at 820°C. However, it can be seen from

Figure 2-11 that precipitate coarsening is very slow at 820°C. Furthermore, the microstructures presented show no gross segregation at this low temperature. In every case, laboratory samples were small and thus heated up and cooled rapidly. At any point in fabrication when laboratory material was taken above 900°C, it cooled rapidly, even without quenching. The slowest cooling rate computed for laboratory material at 700°C is 2.5°C/sec for air-cooled forgings; thus, laboratory material spent less than 20 seconds in the critical coarsening and segregation temperature range, 850 to 900°C, upon cooling. During heating to a forging or solution temperature of 955°C (used for some laboratory ingots), laboratory ingots spent more time in the critical temperature region than they did on cooling. Because ingots were only 5 cm in diameter (and all other samples were smaller), heatup was fairly rapid; some coarsening on heatup could be expected, however. In fact, laboratory material quenched from a 1-hour solution treatment at 955°C did show a few particles as large as 1 to 2 μ ; this is evidence that particles as large as 5 to 6 μ may have existed before the solution treatment (Figure 2-16).

The first batch of vendor material showed particles as large as 5.5μ in diameter and a nonuniform banding of these particles. Reference to the process history and to Figures 2-11 and 2-16 leads to an explanation for this observation. The tubing was annealed for a total of 13 hours at 760°C ; this would be expected to increase particle size by about 0.8μ , but could not be responsible for the largest particles. Extrusion was performed below 760°C and was not a major contributor to precipitate coarsening. The extrusion billets were solution-treated at 1000°C , but the total residence time in the furnace was only 1 hour. The quench-cooling rate at 700°C was computed at $28^{\circ}\text{C}/\text{sec}$ at least; therefore, the large precipitates were not likely to have been formed during this quench. Large particles and an inhomogeneous structure must have developed before, and persisted during, the solution treatment. The material was forged at " 900 to 1015°C " and at " 844°C ," was slow-cooled at least twice, could well have dropped below 900°C during the forging operation, and, because of its size, heated up very slowly. Very large particles and two-phase segregation would be expected. During the "1-hour" solution treatment, the particles were actually growing until the extrusion billets slowly reached temperatures above 900°C . The time actually at temperature was too short to take the largest particles into solution and to homogenize the microstructure completely. Most of the particles should have gone into solution, and slight variations (among billets and along a single billet) in heatup rate, actual temperature, and residence time could well have been responsible for the variable performance of this batch of material.

For large vendor-scale material, it is essential that a solution treatment of several hours be performed at 1000 to 1050°C after any operations in which the material is heated up through the 850 to 900°C critical region. Cooling into the two-phase region is also to be avoided during forging on cold dies (after removal of the forging from the soaking furnace) since this could lead to segregation.

Clearly, the alpha-plus-beta region is to be avoided, and sufficient time at 1000 to 1050°C is required to redissolve precipitates formed on heating large-scale billets. After solution, rapid cooling through the two-phase region is required.

These precautions alone should assure good corrosion behavior; i.e., behavior similar to that for Zircaloy-2. However, to obtain corrosion behavior near the potential for the Zr-Cr alloy, it is necessary to age the solution quenched material in a certain way at temperatures below 800°C . It is necessary to age the quenched alloy to relieve lattice strain; but the quenched alloy, if over-aged, will perform poorly due to over-depletion of chromium in solid solution. The practical requirement for intermediate anneals during tubing cold reduction and the difficulty of maintaining dimensional tolerances on finished tubes during a solution quench also center attention on the alpha phase time-temperature-cold-work parameters.

2.3 STATISTICAL FABRICATION SCHEDULE STUDY

A statistically designed study of fabrication variables had been taking place in parallel with the studies just described. The study was made on tensile/corrosion coupons cut from 0.127-cm sheet fabricated by 27 separate schedules from 1.8-kg , consumable, arc-melted, sponge-base ingots. Since, as just discussed, such ingots cool at about the same rate as full-scale billets during quenching, half of this study was somewhat academic. Half the material studied was quenched after forging at cooling rates much faster than could be obtained for full-scale tubing billets. The study of the other, non-quenched ingots did, however, throw some additional light on the important matter of the effect of alpha phase time-temperature-cold-work parameters on maximizing the corrosion resistance of material treated to avoid precipitate particle coarsening in the two-phase temperature range (800 to 900°C). Furthermore, the statistical study considered the effect of alpha phase process parameters on mechanical properties and hydrogen pickup, as well as on corrosion rates at 400 and 500°C in high-pressure, refreshed, oxygenated steam.

The results of this statistical study were that after solution treatment and rapid cooling, corrosion behavior was not extremely sensitive to alpha phase processing within the range of parameters studied:

Lab	Full-Scale Translation	
Forging	Extrusion temperature	$780, 820, 955^{\circ}\text{C}$ (2-1/2 hours)
Hot Rolling	Intermediate anneals	$540, 635, 760^{\circ}\text{C}$ (2 hours)
Final	Stress relief anneal	$480, 600, 760^{\circ}\text{C}$ (2 hours)

Mechanical properties were sensitive to the final annealing temperature, as expected. Statistical analysis (Ref. 6) of the data from nonquenched ingot suggested the following "best" parameters:

Extrusion temperature	780°C (or lower) (2-1/2 hours)
Intermediate anneals	595°C (2 hours)
Stress relief anneal	480°C (or lower) (2 hours)

Since these results were obtained on laboratory melts, the "best values" were used only as a starting point for studies on actual vendor material. Further exploration of alpha phase parameters was possible on samples cut from early-stage vendor material while the vendor fabrication (which ultimately produced fuel cladding tubes) continued in parallel.

2.4 STUDIES ON VENDOR IN-PROCESS MATERIAL

Samples of the actual vendor material in process for the final batch of tubing were fabricated in the laboratory to sheet by several alternate schedules. Cooling rates, reductions in area, and process times were controlled to simulate known or anticipated vendor conditions. Metallographic, chemical, mechanical, and corrosion test data were taken on coupons from the resultant sheet material. Starting samples of vendor material for these studies were taken at various steps in the tubing process: (1) ingot material; (2) forged, solution-treated, and quenched material; and (3) extruded material. (The fabrication details at each step in the vendor process are given in Section 3 of this report.) These laboratory tests on in-process material led the actual process for tubing. Modifications in the subsequent steps in the reference tubing fabrication process were made as a result of the studies on vendor material.

Six fabrication schedules used in the laboratory simulations on vendor material are referred to by code throughout the discussion that follows. The codes used are summarized in Table 2-8, for reference. Code LAB was found best for fast cooling laboratory ingots; code 240 was suggested by the physical metallurgy and statistical test results; code VP was the vendors' suggested preference for ease in processing; code POR was a compromise schedule discussed; and code NRP was an intermediate step toward the final vendor process.

2.4.1 INGOT COMPOSITION

A slab, 25.4 cm in diameter and 6.4 cm thick, was cut from the vendor-melted ingot and shipped to the laboratory. Samples were taken for chemical analysis and compared with vendor analyses from various points along the ingot.

Both results agreed, and confirmed that the requested composition and impurity limits were met. (Refer to the following sections for the chemical analysis values for the final tubing.)

As a double check on the analyses, a sample of the ingot slab was remelted in the laboratory and processed to sheet by the code LAB schedule (see Table 2-8). A corrosion test of coupons from this sheet (at 500°C in high-pressure, refreshed, oxygenated steam for 1058 hours) gave excellent results: 140 mg/dm² weight gain. The ingot was released for further processing.

2.4.2 SOLUTION TEMPERATURE

To explore the role of solution temperature (see Table 2.8 for various values proposed), samples—6 x 3 x 3.5 cm of vendor ingot—were solution-treated at different temperatures for either 2 or 4 hours, air-cooled (to simulate water quenching of actual thick sections), and aged at 775°C for 4 hours. The results of the 500°C corrosion test are presented in Table 2-9.

No significant effect of solution treatment of the vendor ingot was observed; the solution treatment preferred by the vendor was approved.

2.4.3 QUENCHING

The effect of cooling rate on solution-treated material was explored. The results are given in Table 2-10. Faster cooling increased corrosion in the as-cooled condition. However, aged samples showed the best corrosion resistance for fast-cooled material. Since more rapid cooling rates were shown desirable, the tubing process was changed to include a second quench of the rough-machined extrusion billets; a 2.5-cm hole in the billets allowed water to be circulated through the center of the (smaller) mass of alloy and resulted in a calculated 50% increase in cooling rate. (Rod billets for end plug stock were not double-quenched.)

2.4.4 EXTRUSION TEMPERATURE - ALPHA AGING

From the data in Table 2-10 it appeared that higher temperature aging was advantageous. This observation was further substantiated by the results given in Table 2-11 for coupons cut from the actual quenched vendor billets ready for extrusion. However, a long-term corrosion test was in progress, which gave lower corrosion rates than those for the best samples in Tables 2-10 and 2-11. This more successful test was performed on coupons fabricated from ingot material by the three processes: code 240, code VP, and code POR. Code VP had the lowest upper alpha processing temperature, but VP coupons showed the best

TABLE 2-8
VARIOUS FABRICATION SCHEDULES INVESTIGATED

CODE USED IN TEXT	LAB	240	VP	POR	NRP	FINAL PROCESS
FORGING TEMPERATURE (80% Reduction)	955°C	1025°C	1050°C	1025°C	1050°C	1050 to 900°C
SOLUTION TREATMENT	1 to 2 h 955°C Quench in water (80°C/min.)	2 h 1050°C	20 min. 1050°C	2 h 1040°C	20 min. 1050°C	1 h 1050°C Quench in water (10°C/min.)
<hr/>						
50% Reduction						90% Reduction
EXTRUSION (Hot rolling in Laboratory)	3.3 h total heat and soak 605°C	3 h total heat and soak 780°C	4 h total heat and soak 650°C	1 h Billet Soak 774°C Plus 4 h heat and soak 705°C	4 h total heat and soak 650°C	4 h total heat and soak 650°C
INTERMEDIATE ANNEALS	40% cold work Before one anneal 2 h 760°C	40 min. each 595°C	4 h each 705°C	3 h each 594°C	4 h each 675°C	55% cold work/pass 4 reductions; 3 anneals 705°C
FINAL STRESS RELIEF	(None)	2 h 480°C	6 h 495°C	6 h 476°C	6 h 466°C	6 h 470°C

corrosion behavior at 300, 400, and 500°C in 2500-hour steam tests. The 500°C corrosion rates were: code VP, 2.3 mdd; code POR, 2.9 mdd; and code 240, 3.5 mdd. (Compare 0.8 to 1.9 mdd for lab melts, and 9.6 mdd for the best Zircaloy-2.) The material on test in the three-schedule comparison was cold-worked to simulate

tubing fabrication, while the samples giving data suggesting a higher extrusion temperature were not cold-worked.

It was reasoned that cold work would be expected to promote over-aging, and since over-aging would degrade corrosion resistance, the lower extrusion temperature, 650°C, was approved.

TABLE 2-9
EFFECT OF SOLUTION TEMPERATURE ON Zr-Cr
WEIGHT GAINS IN 500°C STEAM

Solution Treatment*	Average** Weight Gain (cm/cm ²) After					
	355h	433 h	1058 h	1714 h	2699 h	3416 h
955°C - 2 h	146	191	339	466	674	818
955°C - 4 h	147	190	340	463	667	804
1000°C - 2 h	151	192	331	453	663	800
1000°C - 4 h	156	201	354	482	686	830
1050°C - 2 h	149	191	331	451	654	793
1050°C - 4 h	154	198	349	471	682	820

* All samples aged 4 hours, 775°C, after air-cooling small coupons.

** Three coupons each condition. Standard deviation for each value is $\pm 3\%$ of the value. Coupons cut from vendor ingot material.

TABLE 2-10
THE EFFECT OF COOLING RATE ON Zr-Cr
WEIGHT GAINS IN 500°C STEAM

Condition*	Average** Weight Gain (mg/cm ²) After				
	625 h	1281 h	1904 h	2266 h	2983 h
Water Quenched	460	737	979	1127	1355
Plus 12 hours 675°C	192	315	445	541	662
Plus 12 hours 705°C	160	282	408	497	613
Plus 4 hours 775°C	155	200	368	468	548
Oil-Interrupted Quench	371	643	891	1039	1282
Plus 12 hours 675°C	191	325	455	556	690
Plus 12 hours 705°C	172	288	427	524	642
Plus 4 hours 775°C	158	254	372	477	566
Air Cooled	255	431	586	821	884
Plus 12 hours 675°C	241	393	526	649	781
Plus 12 hours 705°C	229	379	512	636	762
Plus 4 hours 775°C	204	342	471	589	710

* All samples solution treated 4 hours 1050°C.

** Average two samples; standard deviation for each value about $\pm 5\%$. Coupons cut from vendor ingot material.

TABLE 2-11
EFFECT OF AGING TREATMENT ON Zr-Cr
WEIGHT GAINS IN 500°C STEAM

Aging Treatment *	Average** Weight Gain (mg/dm ²) After				
	558 h	1181 h	1543 h	1756 h	1852 h
Single Water-Quenched Rod Billet					
780°C - 3 h	134	233	346	440	453
775°C - 1 h	134	279	385	462	477
732°C - 12 h	142	262	390	495	515
705°C - 12 h	145	306	420	513	533
676°C - 12 h	158	336	441	569	584
650°C - 12 h	161	352	465	599	614
650°C - 4 h plus 620°C - 12 h	162	390	453	573	592
650°C - 4 h plus 593°C - 12 h	170	358	466	601	622
620°C - 12 h	179	372	500	641	666
593°C - 12h	172	373	504	652	675
Double Water-Quenched Tube Hollow					
780°C - 3 h	134	222	354	432	448
775°C - 1 h	140	275	388	461	478
732°C - 12 h	133	218	348	438	451
705°C - 12 h	152	309	416	511	530
676°C - 12 h	139	321	430	562	583
650°C - 12 h	171	352	480	597	615
650°C - 4 h plus 620°C - 1 h	152	315	440	552	573
650°C - 4 h plus 593°C - 12 h	168	339	474	594	614
620°C - 12 h	169	339	459	588	605
593°C - 12 h	189	374	512	650	669

* Coupons cut from quenched vendor material ready for extrusion.
 (1050°C forging and solution temperature; quenched as indicated)

** Two coupons each condition; average deviation about $\pm 7\%$ on each value.

2.4.5 TUBE REDUCTION (COLD WORKING) AND INTERMEDIATE ANNEALING (ALPHA AGING)

Because the code VP fabrication schedule, although the best tested on vendor starting material, was not giving corrosion rates quite as low as laboratory material (code LAB), and because of the reasoning previously stated, lower intermediate annealing temperatures were considered (code NRP). The two cases were compared by corrosion testing at 400 and 500°C. Starting with material cut from quenched extrusion billets, the fabrication was finished by code VP and code NRP schedules. The results, given in Table 2-12, showed little difference between 705°C (VP) and 675°C (NRP) intermediate annealing temperatures.* The 705°C temperature was acceptable for processing the tubing.

* It will be shown that final stress relief temperature has little or no effect on corrosion behavior.

(Both cases gave lower weight gains than VP, POR, or 240 material processed starting from ingot; i.e., the modification giving more rapid quenching of extrusion billets was beneficial.)

After extrusion, three extrusion blanks were annealed at 705°C, and the first cold reduction (rocking) pass was attempted. All three tubes cracked. It was later discovered that the cracking was caused by exaggerated grain growth in the extrusion blank anneal due to residual cold work from the 650°C extrusion. The problem was circumvented by omitting the anneal before the first rocking pass, limiting the reduction in the first passes to 55%, and adding a final 60% pass.

TABLE 2-12
EFFECT OF FABRICATION SCHEDULE OF QUENCHED VENDOR MATERIAL
ON WEIGHT GAINS IN 400 AND 500°C STEAM

Fabrication Schedule	Average* Weight Gain (mg/dm ²)							
	400°C				500°C			
	98 h	656 h	1279 h	2475 h	98 h	656 h	1279 h	1950 h
Single Quench								
Code NRP**	18	35	45	62	57	107	146	304
Code VP**	16	28	38	55	54	106	152	332
	558 h	1181 h	2377 h	558 h	1181 h	1852 h		
Double Quench								
Code NRP**	30	41	58	97	140	231		
Code VP**	25	35	52	95	146	313		

* Six coupons; standard deviation about $\pm 3\%$ of each value.

** See text for parameters.

Fabricated from material out from quenched vendor material ready for extrusion.

Before the problem of exaggerated grain growth was diagnosed, tests were run to explore higher annealing temperature on the premise that this would permit higher rocking reductions per pass. The results in Tables 2-13 and 2-14 show that annealing temperatures above 705°C made little difference in 400°C steam corrosion behavior but were detrimental to 500°C steam corrosion resistance of the quenched vendor material. Thus the choice of 705°C as the intermediate annealing temperature was again

confirmed and was specified for the processing of the fuel cladding tube.

2.4.6 FINAL STRESS RELIEF ANNEAL

Several samples of code POR material had been held aside after the final cold-working step and were stress-relieved for 6 hours at either 466, 496, or 510°C. Tensile tests data taken at 300°C for these samples and for the reference 6 hours at 476°C POR treatment compare as follows:

Stress Relief Temperatures (°C)	Yield (kg/mm ²)	Ultimate (kg/mm ²)	Elongation (%)	Reduction Area (%)
466	20	27	31	82
476	17	27	32	81
496	16	24	41	85
510	16	23	37	83

Corrosion tests in 500°C steam gave the results shown in Table 2-15.

It was concluded that the final stress relief anneal could be taken as 466°C without any significant loss in corrosion

resistance or ductility, but with a measurable increase in yield strength. The tubing process was modified to call for a stress relief anneal of 6 hours at 466°C.

TABLE 2-13
EFFECT OF INTERMEDIATE ANNEALING TEMPERATURES
FOR DOUBLE-QUENCHED VENDOR TUBE BILLET ON
WEIGHT GAINS IN 500°C STEAM

Annealing Sequence*	Average** Weight Gain (mg/dm ²) After				
	288 h	623 h	985 h	1198 h	1294 h
Case 1 705°C 705°C 705°C	89	116	163	223	240
Case 2 705°C 705°C 725°C	90	118	163	223	242
Case 3 705°C 725°C 725°C	93	121	174	234	253
Case 4 725°C 725°C 725°C	87	117	184	272	289
Case 5 705°C 705°C 745°C	90	118	240	248	266
Case 6 705°C 745°C 745°C	92	122	191	277	292
Case 7 745°C 745°C 745°C	103	143	231	330	343

* Simulated extrusion: 3-hour soak at 645°C, 50% RA; three cold-work passes of 55% RA intermediate anneal as indicated; final stress relief anneal: 6 hours at 466°C.

** Four coupons; standard deviation about $\pm 4\%$ each value.

TABLE 2-14
EFFECT OF INTERMEDIATE ANNEALING TEMPERATURES
FOR DOUBLE-QUENCHED VENDOR TUBE BILLET ON
WEIGHT GAINS IN 400°C STEAM

Annealing Sequence*	Average** Weight Gain (mg/dm ²) After				
	288 h	623 h	1534 h	1699 h	1819 h
Case 1 705°C 705°C 705°C	22	30	45	51	52
Case 2 705°C 705°C 725°C	24	32	46	53	54
Case 3 705°C 725°C 725°C	25	33	47	53	54
Case 4 725°C 725°C 725°C	24	31	46	52	53
Case 5 705°C 705°C 745°C	21	29	42	49	49
Case 6 705°C 745°C 745°C	20	28	41	48	48
Case 7 745°C 745°C 745°C	25	33	47	54	55

* Simulated extrusion: 3 hours soak at 645°C, 50% RA; three cold-work passes of 55% RA intermediate anneal as indicated; final stress relief anneal: 6 hours at 466°C.

** Four coupons; standard deviation about $\pm 4\%$ each value.

TABLE 2-15
EFFECT OF FINAL STRESS RELIEF TEMPERATURE ON Zr-Cr
WEIGHT GAINS IN 500°C STEAM

Stress Relief Temperature*	Average** Weight Gain (mg/dm ²) After				2983 h
	625 h	128 h	1904 h	2266 h	
466°C	120	198	262	315	402
496°C	115	190	258	301	392
510°C	114	188	251	301	392

* Six hours anneal; vendor ingot material fabrication process code POR up to stress relief.

** Four coupons each value; standard deviation about $\pm 3\%$ of each value.

3. TUBE FABRICATION

As a result of earlier experience, the process used for fabrication of the Zr-Cr tubing was carefully controlled. The details of the various steps in the tubing process are presented.

3.1 MELTING

The Zr-Cr ingot was vacuum melted by Wah Chang Corporation, using a consumable-electrode arc furnace. Chromium powder and zirconium chunklets were pressed into rectangular bars 4.6 x 6.9 x 69 cm long (2 x 3 x 30 inches long). These bars were then electron-beam-welded end to end, to make up the initial electrode. This electrode was first vacuum-melted to form an 8-in.-diameter ingot and then revacuum-melted into a 28-cm-(11 in.) diameter ingot. The unconditioned ingot weight was 452 kg (973 lb). The ingot was conditioned by machining 1.7 cm (3/4 in.) from the outside surfaces, resulting in a 24-cm-(9.5-inch) diameter by about 122-cm-(4 ft) long finished ingot. The chemical analysis of the ingot is given in Table 3-1.

Additional chrome was added to the original melt, 1.5 wt% Cr, to allow for evaporation during melting. Approximately 0.24 wt% Cr was lost during melting. The as-cast structure, Figure 3-1(a), exhibits complete macrohomogeneity. On a finer level, Figure 3-1(b), microsegregation is clearly evident (different etching characteristics resulting in dark and light areas shown in micrographs).

3.2 HOT WORKING AND SOLUTION HEAT TREATMENT

As mentioned earlier, hot working in the two-phase region, 800 to 900°C, or slow cooling through this region after hot working should be avoided. The ingot was preheated at 1050°C for 1-1/2 hours, and then hot forged to a 11.4-cm (4-1/2-inch) round. Frequent reheating, every 30 minutes, to 1050°C was required to maintain the surface temperature above 900°C. Without intermediate cooling, the entire forging was solution-treated at 1050°C for 1 hour and then water quenched. All thermal and forging treatments were performed in air. The surface oxide of the final forging was clear and black (Figure 3-2), indicating that only minor surface contamination occurred during the hot-working and solution operations.

One end of the ingot was forged down to 7.9-cm-(3-1/8-in.) diameter by 76-cm-(3-ft) long rod billets. Three rod billets were machined and warm-extruded without any further solution heat treatments. The tube billets were rough-machined from the 11.4-cm (4-1/2-in.) forging to 10.2 cm (4 in.) o.d. x 1.9 cm (3/4 in.) i.d. x 25.4 cm (10

in.) long. These rough billets were then given an additional solution heat treatment at 1050°C for 1 hour at temperature, followed by a water quench on both inside diameter and outside diameter. The as-quenched microstructure (Figure 3-3) exhibited a fine Widmanstätten structure typical of beta-quenched zirconium alloys, with only a minor surface layer about 0.25 mm (0.01 in.) deep which etched differently, probably because of oxygen and nitrogen contamination. Prior beta grain boundaries were clearly retained and selectively etched, indicating a composition or structural difference at the boundary. Evidence of these beta boundaries remained, even after extrusion and subsequent tube reduction and annealing. No coarse precipitates greater than 0.5μ were observed. Final machining of the extrusion billets removed 2.54 mm (0.100 in.) from each surface, resulting in contamination-free billets. A typical hardness traverse (Figure 3-4) shows a large radial hardness variation across the billets before extrusion. This variation could come from two sources: (1) matrix distortion strain caused by shear type beta to alpha transformation, and (2) elastic strain caused by chromium in solid solution. Both sources of hardening are increased by increasing quenching rates from beta solution treatment.

3.3 EXTRUSION

All extrusion billets were jacketed in copper and preheated at 650°C for 2-1/2 hours. Warm extrusion was readily accomplished at 650°C with 25% more ram pressure — 612 metric tons of force (675 tons) — than normally used for the Zircalloys. The reduction ratio was 9 to 1. One initial extrusion attempt at 635°C and normal pressure was abandoned when the material did not start through the die. Impact starting was subsequently used to reduce the possibility of stalling the press. Total time for extrusion was less than 4 seconds. The extruded tube shell size was 4.13 cm (1-5/8 in.) o.d. by 0.8 cm (5/6 in.) wall by 2 to 2.3 meters (8 to 9 ft) long.

Metallographic examination of end sections from various extrusions (Figure 3-5) showed a generally fine-grain alpha structure with a limited amount of grain growth. These large grain areas indicate that the mechanical and thermal conditions were correct in localized regions during extrusion for an exaggerated grain growth phenomenon to start. Hardness measurements indicated a fairly high but relatively constant hardness of 92R_B across the nose of each extrusion. The tail had similar high hardness on the outside diameter, but a lower hardness of 85R_B near the inside diameter. The lower hardness values were related to an increase in grain size (Figure 3-5).

(a)

100X

(b)

750X

Figure 3-1 As-Cast Commercial Zr-Cr Ingot No. 2

GEAP-10044

Figure 3-2 Tapered Section from Zr-Cr Forging after First Solution Treatment

(a) AREA NEAR OUTSIDE SURFACE, 100X

(b) AREA AT INSIDE SURFACE. 100X

Figure 3-3 Microstructure of Zr-Cr Extrusion Billets after Hot Forging and Double Solution Treatment

Figure 3-4 Hardness Traverse Across the Wall of Quenched Extrusion Billet

(a)

OUTSIDE SURFACE OF EXTRUSION
WHERE HARDNESS WAS 95 R_B

100X

(b)

INSIDE SURFACE OF EXTRUSION
WHERE HARDNESS WAS 87 R_B

100X

Figure 3-5 Typical Microstructure of As-Extruded Zr-Cr

TABLE 3-1
CHEMICAL COMPOSITION OF VENDOR INGOT NO. 2

Element	Specification	VNC	
		Laboratory Analysis (sheet) Alloy Additions (wt. %)	Vendor Analysis (ingot)*
Cr	1.10-1.30	1.16 ± 0.02	1.26 ± 0.02
Fe	0.09-0.11	0.111 ± 0.002	0.106 ± 0.002
	(ppm)	Impurities (ppm)	(ppm)
Ni	<70	23 ± 5	10
N	<60	30 ± 2	44 ± 2
O	900-1500	1170 ± 10	955 ± 55
H	<25	11 ± 1	6 ± 1
Al	<75	45 ± 3	49 ± 7
C	<500	135 ± 8	127 ± 3
Si	<120	91 ± 5	<40
Sn	--	<10	55 ± 20
Cu	<50	20 ± 1	<25
Pb	<130	22 ± 2	6 ± 2
Mg	<20	6 ± 1	<10
Mn	<50	12 ± 1	<10
W	<100	<50	25 ± 1
Ti	<50	6 ± 1	<20
Ci	<20	<10	<20
B	<0.5	0.5	0.2
Cd	<0.5	<0.5	<0.3
Co	<20	<2	<5
Hf	<100	<50	80 ± 6

* Vendor also gives Ca <10, Cb <100, Mo <10, Ta <200, U <0.5, V <5, and Zn <50.

Following extrusion, the copper jacket was removed by dissolution in nitric acid, and the outside diameter surfaces were belt-polished to remove surface irregularities.

3.4 COLD REDUCTION

Cold reduction was accomplished by using a 3.8-cm-(1-1/2 in.) tube reducer. Four reductions greater than 50% reduction in area were completed without major difficulty. A minor surface cracking (crazing) was encountered during each of the four reductions. This crazing appeared after rather small amounts of reduction, about 15%, and the number of cracks increased with continued reduction to 60%. The depth of individual cracks was less than about 0.038 mm (0.0015 in.) and generally appeared rounded at the crack tips. (This condition is not unique to the Zr-Cr alloy but has been observed on titanium alloy and Zircaloy tubing.) In most cases, the crazing was removed by etching

the reduced tubes before annealing. Before the final sizing reduction, the inside diameter of all the tubes was etched to minimize the inside diameter cracks. After the last reduction, belt-polishing was employed to remove about 0.076 mm (0.003 in.) from the outside diameter of the tubing to ensure a crack-free surface before final etching.

All intermediate annealing and final stress relief were performed in vacuum, less than 10^{-4} torr. All tubes were bright after each anneal. The bright surface turned brown after standing in air at ambient temperature, about 25°C. The brown surface film was readily removed in standard HNO_3 -HF etching solutions after each reduction.

After etching, the Zr-Cr tubing was coated with a light film or stain of very fine particles. These particles were easily removed by wiping with a sponge or scrubbing with a nylon brush. If these particles were not removed after etching, the

possibility of fluoride contamination would be greatly increased.

Each tube was slightly bowed after the final stress relief and required straightening, using a standard three-stand roller straightener. The final tubes were well within the specified straightness tolerance.

4. CHARACTERIZATION OF Zr-Cr ALLOY TUBING AND BAR STOCK

The Zr-Cr alloy that was fabricated into tubing and bar stock for the fuel rod irradiation experiment in the Consumers Big Rock Point (BRP) reactor was carefully characterized to ensure that the potential of the alloy was actually realized on the commercially-produced wrought products. Two tube sizes were fabricated: 0.968-cm (0.380 in.) i.d. x 0.081-cm (0.032 in.) wall for use as fuel cladding, and 1.271 cm (0.501 in.) i.d. x 0.081 cm (0.32 in.) wall for an out-of-pile heat transfer corrosion test. The latter tubing was necessary to facilitate its use as a heater sheath in existing facilities, and this tubing was used for both heat transfer and isothermal corrosion tests. Both corrosion and mechanical tests were performed on the bar stock.

4.1 INSPECTION

A 100% inspection was performed on the Zr-Cr fuel tubes. All tubes met dimensional tolerances. Inside diameter measurements were within the specified 0.968 ± 0.005 cm (0.379 to 0.383 in.). Wall thickness measurements were within 0.0736 to 0.0864 cm (0.029 to 0.034 in.). Ultrasonic tests revealed no defects greater than 0.0076 cm (0.003 in.) deep. Tube straightness was within the specified 0.0356 cm/43.2 cm (0.014 in./17 in.) maximum bow. All Zr-Cr fuel tubing was judged suitable for use as fuel cladding.

4.2 CHEMICAL ANALYSIS

The chemical composition of all Zr-Cr wrought products, tubing and bar stock, was checked to verify that no compositional changes had occurred during processing. The results are compared with the ingot analysis and specifications in Table 4-1. No major changes were noted; all wrought products fully met specifications.

4.3 METALLOGRAPHY

Metallography performed on ten samples picked at random showed the fuel tubing to have a uniform fine grain size smaller than ASTM 10 (Figure 4-1). Individual grains were equiaxed in the transverse direction and slightly elongated in the longitudinal direction, typical for rocked zirconium alloy tubing. No large grains, larger than ASTM 10, were

observed in any of the cross sections examined. Background signals during the ultrasonic testing of this tubing were also representative for homogeneous fine grain material.

Hydrogen content was determined to be < 20 ppm, which is in agreement with the hydrogen analysis made by the hot extraction method, < 20 ppm, hydrogen. The hydride orientation was random (Figure 4-2). Fine alpha grain material with low hydride content was also verified for the bar stock and heat transfer tubes (Figure 4-3).

4.4 CORROSION RESISTANCE

4.4.1 AUTOCLAVE CORROSION TESTS

Corrosion testing of the Zr-Cr tubing and bar stock was performed at 300, 400, and 500°C in three different corrosion facilities. Weight gains for exposures in 300, 400, and 500°C low-flow steam autoclaves (20-23 ppm O_2 + 1 to 3 ppm H_2 added) to 2000 hours are shown in Table 4-2. These data confirm the superior corrosion resistance of all Zr-Cr wrought products as compared to Zircaloy-2 at temperatures above 300°C. The 500°C weight gains are compared to weight gains for sheet made from the best heat of laboratory melts of Zr-Cr alloy in Figure 4-4. Although the corrosion rates for the wrought products were slightly higher than the best laboratory melts, the corrosion rates of the wrought products were quite acceptable.

4.4.2 CORROSION TESTS - CL-1 LOOP

Long-term, out-of-pile corrosion tests were performed on the Zr-Cr tubing in the CL-1 corrosion loop. The specimens accumulated 7800 hours, approximately the same exposure time as the first group of irradiated test rods removed from Consumers Big Rock Point reactor during the June - July, 1968 outage.

The CL-1 simulates the boiling water reactor environment without neutron flux. The flow diagram of the loop is shown in Figure 4-5. The loop was operated at 285°C, 1000 psi, with the saturated water containing approximately 0.2 ppm O_2 and approximately 0.025 ppm H_2 . The steam-water test sections had a 4% steam quality, with the

(1) FIRST NUMBER IS OUTSIDE DIAMETER OF TUBE, SECOND NUMBER IS WALL THICKNESS.

(2) REDUCED TUBES WERE FLASH-ETCHED BEFORE ANNEAL.

Figure 3-6 Flow Diagram of Process Used in Fabrication of Commercial Zr-Cr Tubing

a) TRANSVERSE

100X

b) LONGITUDINAL

100X

Figure 4-1 Typical Microstructure of Zr-Cr Fuel Tubing

100X

Figure 4-2 Typical Cross Section of Zr-Cr Tubing Showing Hydrides

(a)

100X

(b)

100X

Figure 4-3 Typical Transverse Microstructure of (a) Zr-Cr Bar, and (b) Heat Transfer Tubes

Figure 4-4 Steam Corrosion Data, 500°C Exposure

Figure 4-5 Schematic Diagram of the CL-1 Boiling Water Corrosion Test Facility

TABLE 4-1

CHEMICAL ANALYSES OF VENDOR PRODUCTS

<u>ELEMENT</u>	<u>ANALYSIS (wt %)</u>				
	<u>Specification</u>	<u>Ingot*</u>	<u>Fuel Tubing</u>	<u>Heater Sheath Tubing</u>	<u>Bar Stock</u>
Chromium	1.10 to 1.30	1.26 ±0.02	1.29 ±0.05	1.28 ±0.05	1.30 ±0.05
Iron	0.09 to 0.11	0.106 ±0.002	0.105 ±0.002	0.109 ±0.005	0.103 ±0.002
<u>Impurities (ppm)</u>					
Nitrogen	<60	44 ± 2	22 ± 1	24 ± 1	24 ± 2
Oxygen	900 - 1500	955 ± 55	1015 ± 65	1067 ± 80	1068 ± 20
Hydrogen	<25	6 ± 1	17 ± 3	15 ± 2	8 ± 2
Aluminum	<75	49 ± 7	37	37	30
Carbon	<500	127 ± 3	--	--	--
Nickel	<70	10	25	37	24
Silicon	<120	<40	28	28	10
Tin	---	55 ± 20	10	10	10
Copper	<50	<25	18	18	10
Lead	<130	6 ± 2	<5	<5	<5
Magnesium	<20	<10	5	11	7
Manganese	<50	<10	38	38	15
Tungsten	<100	25 ± 1	<50	<50	<50
Titanium	<50	<20	20	20	<5
Chlorine	<20	<20	--	--	--
Boron	<0.5	0.2	<0.2	<0.2	<0.1
Cadmium	<0.5	<0.3	<0.5	<0.5	<0.5
Cobalt	<20	<5	<5	<5	<10
Hafnium	<100	80 ± 6	<50	<50	<50

*Vendor analysis

TABLE 4-2
Zr-Cr TUBING AND BAR CORROSION WEIGHT GAINS
LOW-FLOW STEAM AUTOCLAVES ^(a)

Specimen Description and Initial Condition ^(b)		Average Weight Gain (mg/dm ²)										
500°C Test		24 h	48 h	72 h	144 h	421 h	569 h	966 h	990 h	1579 h	1976 h	2000 h
Zr-Cr Fuel Tube	1	32.7	--	50.5	--	97.4	--	--	130	--	--	205
Zr-Cr Heat Transfer Tube	1	32.4	--	49.6	--	93.4	--	--	125	--	--	246
Zr-Cr Bar Stock	1	--	--	--	--	--	94.5	--	--	167	--	--
Zr-Cr Fuel Tube	2	--	47.0	--	67.8	--	--	129	--	--	239	--
Zr-Cr Fuel Tube	3	21.6	--	38.3	--	81.0	--	--	116	--	--	222
Zircaloy-2 Control	1	74.6	--	105	--	234	--	--	646	--	--	*
400°C Test		72 h	96 h	168 h	341 h	413 h	569 h	910 h	982 h	1587 h	1928 h	2000 h
Zr-Cr Fuel Tube	1	13.2	--	19.9	--	28.7	--	--	41.5	--	--	55.5
Zr-Cr Heat Transfer Tube	1	15.0	--	21.9	--	29.4	--	--	44.2	--	--	57.7
Zr-Cr Bar Stock	1	--	--	--	--	--	27.8	--	--	43.3	--	--
Zr-Cr Fuel Tube	2	--	21.1	--	33.6	--	--	48.9	--	--	60.9	--
Zr-Cr Fuel Tube	3	7.5	--	14.9	--	23.0	--	--	35.3	--	--	49.4
Zircaloy-2 Control	1	19.4	32.0	25.2	42.2	33.2	54.8	67.1	53.8	85.5	95.7	84.3
300°C Test		72 h	96 h	168 h	349 h	421 h	918 h	990 h	1928 h	2000 h		
Zr-Cr Fuel Tubes	1	5.5	--	5.9	--	9.0	--	15.9	--	30.4		
Zr-Cr Heat Transfer Tube	1	5.1	--	5.4	--	8.1	--	15.6	--	31.8		
Zr-Cr Fuel Tube	2	--	2.2	--	6.7	--	16.0	--	35.2	--		
Zr-Cr Fuel Tube	3	1.1	--	1.3	--	2.8	--	8.2	--	20.8		
Zircaloy-2 Control	1	9.5	9.5	11.7	12.9	14.2	15.7	16.6	19.1	19.7		

(a) 20-23 ppm O₂, 1-3 ppm H₂ added.

(b) 1 - Etched and NaOH cleaned.

2 - Etched, NaOH cleaned, and preoxidized at 300°C for 60 hours (2.6 mg/dm²).

3 - Etched, NaOH cleaned, and preoxidized at 400°C for 14 hours (5.9 mg/dm²).

* Disintegrated

steam phase containing 20 ppm O₂ and 2 ppm H₂. The steam in the saturated steam test section contained approximately 23 ppm O₂ and 1-2 ppm H₂.

Zr-Cr tubing and Zircaloy-2 control specimens were placed in the saturated steam coupon test section and the saturated water coupon test section. Heat transfer test specimens of the Zr-Cr tubing operating at 500,000 Btu/h-ft² were placed in the boiling heat transfer test sections. Also, in the boiling heat transfer test sections, just above the heat transfer test specimens and in the steam-water environment generated by the heat transfer test specimens, there were an isothermal Zr-Cr tubing specimen and a Zircaloy-2 control specimen.

The tests were designed to evaluate the corrosion behavior of Zr-Cr alloy tubing with various surface treatments in simulated reactor environments and under heat transfer conditions. Zr-Cr tubing specimens were prepared with the following surface treatments:

- a. Etched and NaOH cleaned;
- b. Etched, NaOH cleaned, and preoxidized at 300°C for 60 hours; and
- c. Etched, NaOH cleaned, and preoxidized at 400°C for 14 hours.

The heater elements required tubing with a diameter larger than the normal fuel tubing; therefore, two different sizes of tubing were fabricated. The tubing, designated as Zr-Cr fuel tubing, was the same tubing used for cladding on the fuel rod irradiated in Consumers Big Rock Point reactor. The tubing designated as Zr-Cr heat transfer tubing received a slightly different fabrication process. The process flow diagram for both the Zr-Cr fuel tubing and the Zr-Cr heat transfer tubing is shown in Figure 3-6. Metallographic characterization of the tubing after fabrication showed that the two tubings had comparable grain size (ASTM No. 11-12), hydride content, and second-phase particle size ($< 1/2 \mu$) and distribution. The only detectable difference was a difference in hardness. The fuel tubing had a hardness of DPH 197 (Rp90.9), compared with a hardness of DPH 185 (Rp88.3) for the heat transfer tubing.

The CL-1 corrosion loop test was terminated after the specimens had accumulated an exposure of approximately 7800 hours. The heat transfer and isothermal steam-water specimens were removed from the loop and thoroughly examined. The specimens had tightly adhering, lustrous, black oxide films. No evidence of gross pitting or post-transition corrosion was observed.

Sections were taken from the center and each end of both the steam-water and heat transfer specimens for metallographic examination. Oxide films were found on the inside surface of all of the specimens. Figure 4-6 shows the films from the center section of a heat transfer specimen. The films on the outside surface of all of the specimens were uniform and tightly adhering. The films on the inside surface varied along the specimens' lengths.

The original weight gains reported in the previous quarterly reports assumed that no oxide film was being formed on the inner tube surface of the specimens. Oxide film thicknesses, on the outer and inner tube surfaces were measured. To correct the previously reported data, a new weight gain has been calculated from the oxide film thickness on the outer surface of the specimens. Figure 4-7 illustrates the original weight gains reported for the specimens, and the corrected outer surface weight gain as determined by oxide film thickness measurements.

Oxide film thickness measurements for Zr-Cr and Zircaloy-2 heat transfer specimens are compared in Table 4.3. The results indicate that in a simulated BWR environment, the corrosion rate of the Zr-Cr alloy is unaffected by the heat transfer conditions up to 7800 hours exposure. In addition, it appears that the Zircaloy-2 and the Zr-Cr alloys have similar corrosion rates under isothermal steam-water environment conditions at 285°C.

Since the gas composition inside the tubes was not known, it was impossible to assess the hydrogen contribution during the growth of the film on the inside surface. Therefore, no attempt was made to determine the hydrogen level in the tubes. However, the hydrogen level was estimated from the hydride content in the metallographic sections to be less than 50 ppm. The hydrides were uniformly disbursed and the orientation was random.

Hardness traverses were performed across the walls of the specimens. No hardness gradient was observed on either the heat transfer or isothermal specimens. The average hardness of the specimens is tabulated as follows:

<i>Specimen Description</i>	<i>Hardness KHN</i>
Zr-Cr heat transfer tubing	
under heat transfer, as etched	188
Zr-Cr heat transfer tubing under heat transfer, preoxidized at 400°C for 14 hours	182
Zr-Cr heat transfer tubing and, isothermal steam-water, as etched	188
Zr-2 control, isothermal steam-water, as etched	182

OUTSIDE SURFACE

Zr-Cr HEAT TRANSFER TUBING UNDER HEAT TRANSFER
 (500,000 Btu/h-ft²)
 SURFACE TREATMENT-AS ETCHED
 EXPOSURE - 7592 hours

Figure 4-6 Oxide Films on Outside Diameter and Inside Diameter Surfaces of Center Section of As-Etched Zr-Cr Heat Transfer Corrosion Specimen

Figure 4-7 Corrected Data on Heat Transfer and Isothermal Steam-Water Corrosion Specimens, CL-1 Corrosion Loop

There was no significant difference between the hardness of the Zr-Cr heat transfer specimens and the Zr-Cr isothermal specimen.

The weight gains of the saturated water and saturated steam corrosion specimens are summarized in Table 4-4. The saturated water specimens have comparable weight gains for both the Zr-Cr tubing and the Zircaloy-2 control specimen. The weight gains of the saturated steam specimens are illustrated in Figure 4-8. The results indicate that:

- The Zr-Cr tubing specimens have higher weight gains than the Zircaloy-2 control. This anomalous behavior is contrary to high-temperature (400°C and 500°C) steam autoclave corrosion results.
- The Zr-Cr fuel tubing specimens have higher weight gains than the Zr-Cr heat transfer tubing specimen. The cause of the higher weight gains of the fuel tubing is not known.
- The preoxidized Zr-Cr fuel tubing specimens have higher weight gains than the etched Zr-Cr fuel tubing (as was the case for the heat transfer heater tubes).

To verify the anomalous behavior of the Zr-Cr tubings in the saturated steam environment and the difference in the weight gain between the Zr-Cr fuel and heat transfer tubing, another set of specimens was prepared from the same lot of material. In addition, specimens were prepared from Zr-Cr swaged and drawn bar stock. The surfaces of the specimens were prepared under laboratory conditions. The new set (designated as the second set of specimens) was run concurrently with the first set of specimens in the CL-1 loop. The only difference was that the isothermal steam-water specimens were located in the steam and water coupon test section instead of directly in line with the heat transfer specimens in boiling heat transfer test sections. The results, after 6992 hours of exposure, are summarized in Table 4-5.

The weight gains of the specimens in the saturated water were lower, but similar to the weight gains of the first set of specimens. The weight gains of the isothermal steam-water specimens were similar to the corrected weight gains of the first set of specimens. The weight gains of the specimens located in the saturated steam environment are illustrated in Figure 4-9. The data indicate the same type of anomalous behavior as the first set of specimens. However, the oxidation rates for the fuel tubing were considerably lower for the second set of specimens. This behavior remains unexplained. As reported in subsequent sections of this report, the anomaly was not reflected in any way in-reactor

on the fuel cladding, but similar anomalies were observed for corrosion coupons mounted in a vented dummy tube.

4.4.3 CONCLUSIONS

The following conclusions may be drawn from the corrosion test results.

- a. Commercially fabricated Zr-Cr alloy tubing has quite acceptable corrosion rates in high-temperature autoclave corrosion tests (300, 400, and 500°C).
- b. The Zr-Cr alloy has excellent corrosion behavior under heat transfer and in the isothermal steam-water environments of the CL-1 corrosion loop (simulated BWR environments). The Zr-Cr alloy's corrosion resistance in these environments is similar to that for Zircaloy-2.
- c. In the CL-1 corrosion loop, the Zr-Cr alloy is unaffected by heat transfer conditions up to 7800 hours of exposure.
- d. The Zr-Cr alloy is sensitive to the saturated steam environment of the CL-1 corrosion loop. The cause of this anomalous behavior is unknown.

4.5 MECHANICAL PROPERTIES

Mechanical properties of fine-grain Zr-Cr tubing were determined by tensile tests on tubing and by burst and stress rupture pressure tests on tubing specimens at various temperatures to be fully adequate for the intended irradiation. The properties measured included: longitudinal tensile properties, burst hoop stress at different strain rates, stress rupture performance, circumferential fracture elongations, and Larson-Miller parameter creep constant.

The mechanical tests were particularly interesting because the Zr-Cr tubes had a very fine-grain size. The grain size of the material tested was ASTM 10 or less [< 0.0127 mm (< 0.5 mil) mean diameter] as compared with ASTM 7 or less [< 0.0304 mm (< 1.2 mil) mean diameter] for normal Zircaloy-2 alloy tubing (Ref. 2).

4.5.1 LONGITUDINAL TENSILE TESTS

Tensile tests were performed on Zr-Cr fuel tubing and bar stock at ambient temperature, and at various temperatures to 600°C (1120°F). These tests (Table 4-6) indicate longitudinal tensile properties similar to stress-relieved Zircaloy-2. Adequate ductility was also demonstrated by total tensile elongations of 20% or greater. Properties for stress-relieved Zircaloy-2 tubing are also shown in Table 4-6 for comparison.

TABLE 4.3
OXIDE FILM THICKNESSES AND CORRECTED WEIGHT GAINS
FOR HEAT TRANSFER AND ISOTHERMAL SPECIMENS

Specimen Description	Initial Surface Condition (a)	Loop Environment	Oxide Thickness (Microns)								Measured Wt. Gain (Mg/dm ²) (b)		Weight Gain Calculated (d) From O.D. Oxide Thickness Mg/dm ²
			End	I.D. Center	End	O.D.			Avg	7592h	7863h		
						End	Center	End					
Zr-Cr Heat Transfer Tubing Under Heat Transfer	1	280°C (536°F) to 285°C (546°F) at 514,500 (e) Btu/h-ft ²	6.7	2	4	1	1	1	1.0	56.6		15.6	
Zr-Cr Heat Transfer Tubing Under Heat Transfer	3	280°C (536°F) to 285°C (545°F) at 518,900 (e) Btu/h-ft ²	6.7	2.7	5.3	1.3	1.3	1.3	1.3		54.8	13.4 (c)	
Zr-Cr Heat Transfer Tubing	1	285°C (548°F) Isothermal (e) Steam-Water	0.3	0	0	0	1	1	1.0		22.2	15.6	
Zr-2 Control	1	285°C (546°F) Isothermal (e) Steam-Water	0.4	0.5	0.4	1	1	0.9	1.0		23.3	15.6	

- (a) 1 - Etched and NaOH cleaned.
 2 - Etched, NaOH cleaned, and preoxidized at 300°C for 60 hours (2.6 mg/dm²).
 3 - Etched, NaOH cleaned, and preoxidized at 400°C for 14 hours (5.9 mg/dm²).
 (b) For preoxidized specimens, preoxidation weight gain is not included
 (c) Corrected for preoxidation weight gain of 6.9 mg/dm².
 (d) A factor of 15.6 mg/dm²/micron was used to convert oxide film thickness to weight gain.
 (e) Water phase in 0.2 ppm O₂ and 0.025 ppm H₂.
 Steam phase in 20 ppm O₂ and 1-2 ppm H₂.

Figure 4-8 Out-of-Pile CL-1 Loop Saturated Steam Corrosion Test Data on Zr-Cr Alloy Tubing (546°F, 1000 psi). First set of specimens.

Figure 4-9 Out-of-Pile CL-1 Loop Saturated Steam Corrosion Test Data on Zr-Cr Alloy Tubing (546°F, 1000 psi). Second Set of Specimens.

TABLE 4-4

CL-1 LOOP CORROSION TEST RESULTS, FIRST SET OF SPECIMENS

Specimen Description	Initial Surface Condition (1)	Loop Environment	Specimen Number	Average Weight Gain (2) (mg/dm ²)									
				2549h (3)	3149h	4146h	5134h	6134h	7128h	8130h	9134h	10142h	
Zr-2 Control	1	285°C (546°F) Saturated Water (4)	1	16.8	16.6	18.4	19.1	19.6	19.7	20.5	21.1	23.3	
				629h	1229h	2226h	3214h	4214h	5208h	6209h	7213h	8221h	
Zr-Cr Fuel Tubing	1	285°C (546°F) Saturated Water (4)	1	11.9	14.4	17.2	19.4	19.7	20.8	22.6	25.2	26.5	
				271h	600h	871h	1597h	1868h	2535h	2856h	3585h	3856h	4579h
Zr-Cr Fuel Tubing	1	285°C (546°F) Saturated Steam (6)	1	7.4		10.2		19.9		64.1		133	
			2	7.8		16.8		70.7		128		252	
			3	7.8		10.5		17.6		38.6		83.4	
			Avg.	7.7		12.5		36.1		77		156	
Zr-Cr Fuel Tubing	2	285°C (546°F) Saturated Steam (6)	1		9.0		50	145		252		369	
			2		17.6		78.9	174		272		380	
			3		34.0		141	291		439		496	
			Avg.		20.2		90	203		321		497	
Zr-Cr Fuel Tubing	3	285°C (546°F) Saturated Steam (6)	1	19.1		105		243		441		600	
			2	9.4		67.2		186		357		508	
			3	13.7		70.3		224		398		553	
			Avg.	14		81		218		399		554	
Zr-Cr Heat Transfer Tubing	1	285°C (546°F) Saturated Steam (6)	1	7.2		9.9		16.2		30.5		47.6	
Zr-2 Control	1	285°C (546°F) Saturated Steam (6)	1	11.2		12.3		15.7		19.2		19.4	
													21.3
													23.1
													21.9
													20.9

- (1) 1 - Etched and NaOH cleaned.
2 - Etched, NaOH cleaned, and preoxidized at 300°C for 60 hours (2.6 mg/dm²).
3 - Etched, NaOH cleaned, and preoxidized at 400°C for 14 hours (5.9 mg/dm²).
(2) For preoxidized specimens, preoxidation weight gain is not included.
(3) 282°C (539°F) subcooled water 1.5 ppm O₂ in CL-4 loop, transferred to CL-1 loop.
(4) Isothermal section of CL-1 loop with ~0.2 ppm O₂ and ~0.025 ppm H₂.
(5) Saturated steam section of CL-1 loop has 23 ppm O₂ and 1-2 ppm H₂.

TABLE 4-5

CL-1 LOOP CORROSION TEST RESULTS, SECOND SET OF SPECIMENS

Spec. Description	Initial ⁽¹⁾ Condition	No. of Specimens	Environment	Average Weight Gain ⁽²⁾ (mg/dm ²)							
				Preoxidation	997h	1985h	2985h	3979h	4980h	5984h	6992h
Zr-Cr Fuel Tubing	1	3	285°C (546°F) Saturated Water ⁽³⁾	--	8.0	9.6	10.3	10.9	12.1	13.2	13.6
Zr-Cr Fuel Tubing	2	3	285°C (546°F) Saturated Water ⁽³⁾	6.9	3.0	4.6	5.4	6.5	7.3	8.1	9.3
Zr-Cr Heat Transfer Tubing	1	3	285°C (546°F) Saturated Water ⁽³⁾	--	7.8	11.4	11.0	10.9	11.6	13.5	14.7
Zr-Cr Heat Transfer Tubing	2	3	285°C (546°F) Saturated Water ⁽³⁾	6.3	2.5	4.6	5.5	4.5	6.2	7.2	7.8
Zircaloy-2 Tubing	1	3	285°C (546°F) Saturated Water ⁽³⁾	--	8.2	10.4	11.1	11.3	12.4	13.5	14.6
Zircaloy-2 Tubing	2	3	285°C (546°F) Saturated Water ⁽³⁾	10.2	4.5	6.3	7.0	6.7	8.5	10.1	11.1
Zr-Cr Fuel Tubing	1	3	285°C (546°F) Isothermal Steam-Water ⁽⁴⁾	--	7.7	9.8	10.9	11.4	12.6	13.5	14.7
Zr-Cr Fuel Tubing	2	3	285°C (546°F) Isothermal Steam-Water ⁽⁴⁾	6.8	3.0	6.8	6.8	6.4	8.1	8.3	10.0
Zr-Cr Heat Transfer Tubing	1	3	285°C (546°F) Isothermal Steam-Water ⁽⁴⁾	--	8.0	10.2	10.9	12.0	12.0	13.5	14.9
Zr-Cr Heat Transfer Tubing	2	3	285°C (546°F) Isothermal Steam-Water ⁽⁴⁾	5.8	3.1	4.7	4.7	7.1	6.9	8.1	8.8
Zircaloy-2 Tubing	1	3	285°C (546°F) Isothermal Steam-Water ⁽⁴⁾	--	9.1	10.3	10.9	12.2	12.2	13.9	14.9
Zircaloy-2 Tubing	2	3	285°C (546°F) Isothermal Steam-Water ⁽⁴⁾	10.5	4.3	5.8	6.4	6.6	8.6	9.2	10.2

(1) 1 - Etched, NaOH cleaned.

2 - Etched, NaOH cleaned, and preoxidized in 400°C steam 14 hours.

(2) For preoxidized specimens, preoxidation weight gain is not included.

(3) Isothermal section of CL-1 loop with ~0.2 ppm O₂ and ~0.025 ppm H₂ in the water.(4) Heat transfer section of CL-1 loop has 20 ppm O₂ and 2 ppm H₂ in steam phase.(5) Saturated steam section of CL-1 loop has 23 ppm O₂ and 1-2 ppm H₂ in the steam.

TABLE 4-5 (cont'd)

Spec. Description	Initial ⁽¹⁾ Condition	No. of Specimens	Environment	Average Weight Gain ⁽²⁾ (mg/dm ²)							
				Preoxidation	997h	1985h	2985h	3979h	4980h	5984h	6992h
Zr-Cr Fuel Tubing	1	3	285°C (546°F) Saturated Steam ⁽⁵⁾	--	17.9	60.9	119	181	258	340	424
Zr-Cr Fuel Tubing	2	3	285°C (546°F) Saturated Steam ⁽⁵⁾	7.1	35.2	107	186	281	420	540	648
Zr-Cr Heat Transfer Tubing	1	3	285°C (546°F) Saturated Steam ⁽⁵⁾	--	10.6	24.9	52.8	85.2	125	175	230
Zr-Cr Heat Transfer Tubing	2	3	285°C (546°F) Saturated Steam ⁽⁵⁾	6.3	22.6	51.3	119	183	259	344	426
Zircaloy-2 Tubing	1	3	285°C (546°F) Saturated Steam ⁽⁵⁾	--	7.8	10.2	10.5	10.6	12.1	13.3	13.9
Zircaloy-2 Tubing	2	3	285°C (546°F) Saturated Steam ⁽⁵⁾	8.7	4.6	6.0	7.6	6.9	8.0	8.7	9.1
				<u>1000h</u>	<u>1994h</u>	<u>2995h</u>	<u>3999h</u>	<u>5007h</u>			
Zr-Cr Bar Stock, Swaged	1	2	285°C (546°F) Steam-Water ⁽⁴⁾	7.3	8.5	10.7	9.9	11.4			
Zr-Cr Bar Stock, Drawn	1	1	285°C (546°F) Steam-Water ⁽⁴⁾	--	7.3	11.5	10.9	12.5			

(1) 1 - Etched, NaOH cleaned.

2 - Etched, NaOH cleaned, and preoxidized in 400°C steam 14 hours.

(2) For preoxidized specimens, preoxidation weight gain is not included.

(3) Isothermal section of CL-1 loop with ~0.2 ppm O₂ and ~0.025 ppm H₂ in the water.(4) Heat transfer section of CL-1 loop has 20 ppm O₂ and 2 ppm H₂ in steam phase.(5) Saturated steam section of CL-1 loop has 23 ppm O₂ and 1-2 ppm H₂ in the steam.

TABLE 4-6
MECHANICAL PROPERTIES OF Zr-Cr TUBING AND BAR

Material	Type of Sample	Test Temp.		0.2% Offset Yield Stress ⁽¹⁾		Ultimate or Burst Stress ⁽²⁾		Elongation		Red. in Area (%)
		(°C)	(°F)	(psi)	(kg/mm ²)	(psi)	(kg/mm ²)	Uniform	Total	
								(%)	(%)	
Bar Stock	Long. Tensile	25	77	67,000	46.8	90,600	63.3	9.0	23.4	49
Fuel Tube	Long. Tensile, Entire Tube	25	77	65,300	45.6	90,500	63.2	---	19.4	---
Fuel Tube	Long. Tensile, Cut Section	25	77	69,500	48.5	90,900	63.5	7.7	14.3	42
Bar Stock	Long. Tensile	100	212	58,000	40.5	79,000	55.1	9.1	24.4	54
Fuel Tube	Long. Tensile, Cut Section	100	212	60,000	41.9	79,500	55.5	10.4	22.1	45
Bar Stock	Long. Tensile	200	392	48,700	34.0	64,800	45.3	7.5	32.5	61
Fuel Tube	Long. Tensile, Cut Section	200	392	50,600	35.4	66,400	46.3	7.3	18.0	45
Bar Stock	Long. Tensile	300	572	41,200	28.8	54,400	38.0	7.5	27.2	68
Fuel Tube	Long. Tensile Cut Section	300	572	45,800	32.0	55,200	38.6	4.3	16.3	53
Fuel Tube	Long. Entire Tube	343	650	33,000	23.1	43,600	30.5	---	22.4	---
Bar Stock	Long. Tensile	400	752	37,000	26.0	44,300	31.0	5.7	37.4	79
Fuel Tube	Long. Tensile, Cut Section	400	752	35,000	24.4	42,800	30.0	4.2	20.4	65
Bar Stock	Long. Tensile	500	932	26,200	18.3	30,900	21.6	4.1	51.7	97
Fuel Tube	Long. Tensile, Cut Section	500	932	26,900	18.8	30,200	21.1	2.3	28.3	91
Bar Stock	Long. Tensile	600	1112	15,200	10.6	18,400	12.9	4.8	52.6	100
Fuel Tube	Long. Tensile Cut Section	600	1112	11,400	7.7	14,300	10.0	5.2	57.7	97
Zircaloy-2	Tensile ⁽³⁾	25	77	>60,000	>42	>70,000	>49	---	>16	---
Zircaloy-2	Tensile	343	650	>32,000	>22.5	----	----	---	-----	---

(1) All Tensile Tests at 0.02 min⁻¹ strain rate.

(2) Hoop Stress based on original tube dimensions.

(3) Values for stress-relieved Zircaloy-2.

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4.5.2 BURST TESTS

The mechanical tests essentially consisted of the pressurization of the tubular test specimens at various test temperatures. Burst pressure tests were conducted by increasing the internal pressures at prescribed rates until rupture occurred. The rates were chosen so that the tube test results could be compared with results of longitudinal specimen tests conducted elsewhere. The stress rupture tests were conducted at constant pressures until rupture occurred.

There were three mechanical property values established by these tests: one was the burst hoop stress, the second was the stress rupture performance, and the third was the circumferential fracture elongation of the failed specimens.

The fine-grain Zr-Cr tubing was fabricated into tubular test specimens approximately 12.7 cm (5 in.) long. The tubing size was approximately 1.14 cm (0.450-in.) o.d. and 0.081 cm (0.032 in.) wall thickness.

The tubes were placed in safety containers within furnaces that were maintained at the specified test temperatures, which ranged from 25°C (77°F) to 600°C (1120°F). The temperatures were monitored continuously by use of thermocouples within the safety containers adjacent to the specimens. Argon pressure was applied internally to the specimens either at an increasing rate for burst tests, or at a constant value for the stress rupture tests. The pressure source was a Haskel gas booster in conjunction with a gas receiver to supply pressure without surges. (For some very high rate burst tests at room temperature, hydraulic pressure was utilized.) The specimen test pressure was indicated by pressure gages and monitored by a pressure cell-recorder combination.

The circumferential fracture elongation was determined by pre- and post-test measurements—the former by diameter measurements, the latter by arc length measurements using a narrow thin foil strip of steel.

The results of the burst tests are listed in Table 4-7.

4.5.3 LOADING RATE EFFECT

To evaluate any potential different burst stress performance which may depend on the rate of application of the load, the pressure loading rates were varied in different tests from 0.035 kg/mm²-min (50 psi/min) to 23 kg/mm²-min (33,000 psi/min). For purposes of data evaluation, these were arbitrarily categorized as "fast rates" and "slow rates," with the pressure rate of 0.35 kg/mm²-min (500 psi/min) being the point of separation. For these specimens,

the pressure rate of 0.35 kg/mm²-min (500 psi/min) corresponds to both an elastic hoop stress rate of approximately 2.34 kg/mm²-min (3350 psi/min) and a circumferential elastic strain rate of approximately 0.024%/min.

As shown in Figure 4-10, the burst stresses at the slower rates are approximately 10% less than those at the higher rates. This rate effect is typical of many materials.

Early in the testing program, prior to receipt of the longitudinal tensile test data, it was established that the fine-grain Zr-Cr was stronger than originally expected. At room temperature, the pressure required to burst the tubes exceeded the capacity of the available pneumatic equipment. To obtain data at an early date, two specimens (Nos. 1 and 5) were loaded hydraulically to burst at pressures of approximately 13.5 kg/mm² (19,250 psi). Also, other specimens at 300°C (572°F) (Nos. 2, 7, and 10) were loaded at prescribed rates to the then maximum available pressures of approximately 6.94 kg/mm² (9900 psi). These pressures were maintained at the values shown in Table 4-7 until rupture occurred. The times to rupture at those pressures varied from 7 to 26 minutes. When the equipment was later modified to provide increased pressure capability, these tests were repeated and the results shown in Table 4-7 were obtained.

4.5.4 COMPARISON OF LONGITUDINAL AND TUBE BURST DATA

Data from longitudinal tensile tests of the Zr-Cr tube material shown in Table 4-6 were compared with the results of the burst tests, and are illustrated in Figure 4-11. The longitudinal tests were conducted at strain rates which varied from 0.002%/min to 2.0%/min at most temperatures, and at 0.02%/min at all temperatures. The range of ultimate stress values reported are indicated in the figure by vertical lines.

It can be seen that the ultimate stress values from the longitudinal tests are consistently lower than the burst stress values from the tube tests. This also is expected when considering the biaxial effect of the stresses. To improve the basis of comparison, the longitudinal data were corrected for the biaxial conditions by utilizing an effective stress and assuming isotropic properties. (This means either multiplying the burst hoop stress by 0.866 and comparing it with the longitudinal tensile stress or, as was done here, dividing the tensile stress by 0.866 and comparing the result with the burst hoop stress.) The corrected value was almost identical to the slow rate burst test data. This would appear to indicate that the fine-grain Zr-Cr tubing was nearly isotropic.

TABLE 4-7

FINE GRAIN Zr-Cr ALLOY BURST TEST RESULTS

Specimen No.	Test Temp.		Pressurization Rate			Burst Pressure		Burst Hoop Stress		Circumferential Fracture Elongation (CFE) (%)	Time to Failure (hours)	Remarks
	(°C)	(°F)	F/S*	psi/min	kg/mm ² -min	psi	kg/mm ²	psi	kg/mm ²			
1	25	77	F	24,500	17.1	19,240	13.40	122,800	86.0	8.1	----	Pressurized to 9050 psi. Repressurized hydraulically to failure. -----
5	25	77	F	33,000	23.0	19,260	13.45	122,800	86.0	9.9	----	
6	25	77	F	1,540	1.08	18,620	13.00	118,600	83.0	12.0	----	
15	25	77	F	3,550	2.48	18,250	12.70	107,200	75.0	9.5	----	
8	200	392	S	222	1.55	12,000	8.40	75,000	52.5	14.4	----	-----
30	200	392	F	1,365	0.955	12,720	8.90	81,500	57.0	6.5	----	
2	300	572	S	63	0.044	9,570	6.70	60,900	42.6	11.2	0.12	Pressurized to 9050 psi. Repressurized to 9570 psi and held to rupture. Pressurized to 9900 psi. Held to rupture. ----- Pressurized to 9620 psi. Held to rupture. -----
7	300	572	S	55	0.038	9,900	6.94	63,200	44.4	6.1	0.23	
9	300	572	S	253	0.177	10,770	7.54	68,300	47.8	8.2	----	
10	300	572	F	652	0.45	9,620	6.75	61,600	43.2	1.8	0.43	
14	300	572	F	3,240	2.26	10,920	7.65	69,200	48.5	7.1	----	
3	400	752	S	48	0.033	7,270	5.10	46,300	32.4	10.3	----	-----
11	400	752	F	584	0.41	8,070	5.65	51,600	36.2	14.1	----	
13	500	932	F	725	0.51	5,650	3.96	37,000	25.9	25.2	----	-----
4	600	1112	S	60	0.042	2,475	1.73	15,800	11.1	45.2	----	-----
12	600	1112	F	560	0.39	3,100	2.17	19,300	13.5	32.2	----	

* F/S = Fast or slow rate of pressurization.

Slow rate < 500 psi/min (< 0.35 kg/mm²-min).Fast rate > 400 psi/min (> 0.35 kg/mm²-min).

Figure 4-10 Zr-Cr Fine-Grain Tube Burst Hoop Stress versus Test Temperature

4.5.5 CIRCUMFERENTIAL FRACTURE ELONGATION (CFE)

The circumferential fracture elongation values were established for the specimens, and are illustrated in Figure 4-12. These data indicate a minimum at approximately 300°C (572°F) and then at higher temperatures, an increase of the CFE with increasing temperature. The CFE data do not indicate significant differences associated with fast and slow strain rates, though several slow rate CFE values are higher than corresponding fast rate values. Circumferential fracture elongations from burst tests indicate lower transverse ductility, 10%, compared to longitudinal ductility. However, 10% circumferential fracture elongation under closed-end burst test conditions is considered quite adequate for the proposed fuel cladding application. The results of the stress rupture tests are summarized in Table 4-8.

4.5.6 STRESS RUPTURE VALUES

The stress rupture data are shown in Figure 4-13 for tests conducted at temperatures between 400 and 600°C. In general, these data are consistent. As indicated, the test of specimen 19 was terminated at 1000 hours without failure. Also shown in Figure 4-13 are comparable stress rupture test results reported for cold-worked Zr-2 (Ref. 7) and annealed Zr-2 (Ref. 8).

4.5.7 LARSON-MILLER PARAMETER

The assessment of the stress rupture performance of the Zr-Cr tubing can be improved if a determination of the standard parameters can be made. The Larson-Miller Parameter (LMP), and particularly the constant of the LMP, are typical parameters that are useful for this purpose. The LMP is of the form,

$$\text{LMP} = T (c + \log t_R),$$

where

T = Temperature, °R,
t_R = Time to rupture, hours, and
c = Material constant.

The test conditions were selected to determine the value of c, which best fits the data. The data are shown in Figure 4-14 which contains plots of the applied hoop stress versus

the LMP for values of c of 10, 15, 10, and 25. These data fit the c = 15 curve best. Specimens 20, 22, and 24, tested at approximately 6.65 kg/mm² (9500 psi) hoop stress, were chosen to help determine c. The curve with minimum scatter of these points is that associated with the most probable value of c.

4.5.8 CIRCUMFERENTIAL FRACTURE ELONGATION (CFE)

The CFE values of stress rupture test specimens are illustrated in Figure 4-12. In general, these indicate that over the range of 400°C (752°F) to 600°C (1112°F), the CFE values increase with increasing temperature, and also increase as the time to rupture increases. Also, for the test times investigated the CFE values from rupture tests are consistently larger than those from burst tests.

4.5.9 CONCLUSIONS

The following conclusions may be drawn from this work.

- In general, based on burst and tensile test results, the fine-grain Zr-Cr tube material was stronger but somewhat less ductile than the usual Zircaloy 2 tubing materials. The stress rupture properties of the Zr-Cr were slightly lower than those of the Zircaloy-2 materials.
- Fine-grain Zr-Cr tubing pressurized at circumferential strain rates greater than 0.024%/min burst at hoop stresses approximately 10% greater than those pressurized at lower rates.
- The circumferential fracture elongation (CFE) of the fine-grain Zr-Cr tubing was less than 15% in the temperature range from room temperature to 350°C (662°F). At 400°C (752°F) and higher temperatures, the CFE increased as the temperature was increased.
- The CFE values of the stress rupture test specimens (for the test times evaluated) were usually greater than those of the burst test specimens at the same temperature.
- The constant of the Larson-Miller parameter for the Zr-Cr material is 15.
- The tubing was mechanically adequate for the irradiation test as fuel cladding.

Figure 4-11 Zr-Cr Fine-Grain Biaxial Test Burst Hoop Stress and Longitudinal Test Ultimate Stress Versus Test Temperature

Figure 4-12 Zr-Cr Fine-Grain Circumferential Fracture Elongation versus Test Temperature

Figure 4-13 Zr-Cr Fine-Grain Initial Hoop Stress versus Time to Rupture

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Figure 4-14 Zr-Cr Fine-Grain Hoop Stress versus Larson-Miller Parameter (LMP)

TABLE 4-8

FINE-GRAIN Zr-Cr ALLOY STRESS RUPTURE TEST RESULTS

Tubular Samples									
Specimen No.	Test Temp.		Internal Pressure		Initial Hoop Stress		Time to Failure (hours)	Circumferential Fracture Elongation (CFE) (%)	Remarks
	(°C)	(°F)	(psi)	(kg/mm ²)	(psi)	kg/mm ²			
16	400	752	4,720	3.30	29,950	21.00	29.7	13.0	----
17	400	752	4,000	2.80	25,300	17.70	91.0	19.0	----
18	400	752	2,980	2.08	19,150	13.40	840.4	26.4	----
19	400	752	2,130	1.49	13,600	9.51	>1000	(2.9)	Not failed after 1000 hours; CFE value shown is diametral expansion.
25	400	752	4,000	2.80	24,900	17.40	71.8	19.3	----
20	500	932	1,500	1.05	9,500	6.65	147.9	41.7	----
21	500	932	1,830	1.28	11,720	8.21	52.2	53.8	----
24	535	995	1,500	1.05	9,500	6.65	34.0	41.6	To check Larson-Miller Parameter (LMP) constant.
22	600	1112	1,500	1.05	9,550	6.68	2.7	45.9	----
23	600	1112	1,000	0.70	6,370	4.46	16.4	52.0	----

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5. IRRADIATION PROGRAM

The primary objective of this program was to evaluate Zr-Cr clad fuel in Consumers Big Rock Point power plant to a target exposure of 15,000 to 20,000 MWd/TU average burnup. Zr-Cr clad fuel rods and Zircaloy-2 clad comparison fuel rods were fabricated and positioned in a reload fuel assembly (designated B-1) so that they operated as hot as possible, to evaluate maximum temperature irradiation conditions. Detailed post-irradiation examinations were performed on a group of the Zr-Cr clad fuel rods and Zircaloy-2 clad fuel rods after 8000 MWd/TU bundle average exposure. Although the Zirconium Alloy Design Program is terminated, the irradiation is continuing beyond the bundle exposure of 15,000 MWd/T at program termination, and should reach 20,000 MWd/TU exposure before discharge from the reactor.

5.1 DESCRIPTION OF FUEL RODS AND DUMMY RODS

Two specific materials were used in this experiment:

- a. Commercial Zr-Cr (Vendor Ingot No. 2)
- b. Zircaloy-2 (Heat No. WC-643)

A summary of the Zr-Cr tubing properties was presented in Section 4 of this report.

At the start of the irradiation, Big Rock Point reload fuel assembly B-1 was unirradiated and available at the Big Rock Point site. Twenty-two fuel rods and four nonfueled dummy rods were used in the experiment, and replaced 26 existing Zircaloy-2 clad fuel rods in this bundle.

All 22 fuel rods (Figure 5-1) were similar to the reload fuel design for 2.6% enriched UO_2 pellet type fuel except that 16 were clad with Zr-Cr and 6 with annealed Zircaloy-2.

In the preparation for fuel rod assembly, welding development tests were performed. Samples of material, identified, only as "zirc," were submitted to three separate welders in three different GE-APED welding shops. Welding parameters, including weld box pumpdown, electrode, spacing, power, and speed of travel, were requested. The range of parameters actually used was very wide, and bracketed the normal Zircaloy-2 fuel rod welding parameters.

Two tensile specimens cut from the welded material from each of the three shops were broken at room temperature. All but one broke with good ductility (28 to 61% reduction in area) outside the weld. The one sample which broke in the less ductile weld had been welded at very high power so that the weld zone was as wide as the gauge section of the sheet tensile specimen.

Samples were corrosion-tested. Weight gains for the total samples were acceptable. The corrosion films in the weld region looked blacker and more uniform than those on the base metal. This is always observed for Zircaloy-2 welds also.

Metallography of the welds revealed that the oxide film over the weld was indeed thinner than over the base metal. The microstructure was typical of zirconium alloy welds. No cracks, voids or microporosity were evident.

Nitrogen analyses of samples cut from the weld regions gave 26 ± 5 ppm, 31 ± 8 ppm, and 25 ± 8 ppm, respectively, for the three welder sources. These values are well within the specification of less than 60 ppm.

The overall finding was that very acceptable welds could be made under conditions even less stringent than those for welds of a normal Zircaloy-2 fuel rod to end cap. The tests were on sheet butt welds; the fuel rod end cap joint is designed to make welding easier. Production welds are fully controlled and automatic. For these reasons, the fuel rod welds were made exactly the same for Zircaloy-2 and Zr-Cr rods.

All welds were given helium leak tests and x-ray radiography tests. The Zr-Cr rods and the Zircaloy-2 rods passed both these tests without any indication of flaws.

The external geometry of the dummy rods resembled the reload fuel rods, and they were readily interchangeable with 2.6% enriched fuel rods. Each dummy rod (Figure 5-2) contained seven individual compartments. Three of these compartments were nonvented and could be separated after irradiation for use as burst or stress rupture type specimens. These compartments also contained six tensile specimens in each, mounted on a tantalum rod. The four remaining compartments were vented by holes in the cladding to allow reactor water to come into contact with specimens inside. These specimens were also mounted on a tantalum

UNLESS OTHERWISE SPECIFIED-USE THE FOLLOWING:				107C5326		GENERAL ELECTRIC		107C5326	
APPLIED PRACTICES	SURFACES	TOLERANCES ON MACHINED DIMENSIONS		107C5326		TITLE ASM		FIRST MADE FOR FUEL BUNDLE	
145A5481	✓	FRACTIONS	DECIMALS	DECIMALS	INCHES

NOTES:

1. SCRATCHES, NICKS, ETC. INTRODUCED IN THE TUBING FABRICATION AND HANDLING SHALL NOT EXCEED .003 IN DEPTH.
2. NO MORE THAN 6" TOTAL OF PT. 14 MAY BE USED IN THE UPPER AND/OR LOWER 10% OF FUEL COLUMN OF EACH ROD TO MEET THE SPECIFIED LENGTH.
3. FILL VOIDS WITH GR. A HE (99.995% PURE). HELIUM ESCAPE THROUGH TUBES AND END PLUGS OR WELDED REGIONS SHALL NOT EXCEED 10^{-6} STD. CM³/SEC. OF HELIUM WITH A VACUUM OF 20 MICRONS OF MERCURY.
4. ALL END PLUGS, CONNECTORS, SPRINGS, WAFFERS, AND INTERNAL TUBE SURFACES SHALL BE FREE OF ALL VOLATILE CONTAMINANTS AT ASSEMBLY.
5. OUTSIDE DIAMETER OF END PLUG WELD SHALL NOT EXCEED .468. THICKNESS OF TUBING OR WELD AT WELD ZONE SHALL NOT BE LESS THAN .029.
6. MAXIMUM WATER VAPOR WEIGHT PLUS ALL OTHER GASEOUS PRODUCTS EVOLVED FROM PELLETS WHEN HEATED TO 1650°C SHALL NOT EXCEED 40×10^{-6} LITERS PER GRAM OF UO₂ (AT STANDARD CONDITIONS, 0°C AND 760 MM HG).
7. FUEL WEIGHT (UO₂) PER ROD BETWEEN 1263 GRAMS MINIMUM AND 1320 GRAMS MAXIMUM. EXPECTED AVERAGE WEIGHT PER ROD OF ALL RODS SHALL BE 1297 GRAMS. WEIGHTS OF UO₂ ARE BASED UPON AN AVERAGE "STACKED" DENSITY OF 94.3% OF THEORETICAL, A MINIMUM "STACKED" DENSITY OF 93.3% AND A MAXIMUM "STACKED" DENSITY OF 96.0%.

(G1) (G2)

DESCRIPTION OF GROUPS	REVISIONS	PRINTS TO
G1- ROCKED ZR-2	1. APP. 17 '87 M.H.T.	
G2- ROCKED VALLOY	ADD DWG. NO. ON DT. NO. 14 CHSD MAT'L. CALL OUT 0.314	
APPROVED BY: [Signature]	APPROVED BY: APED	107C5326
DATE: 10/1/84	SAN JOSE	

Figure 5-1 Details of Zr-Cr and Zircaloy-2 Fuel Rods

UNLESS OTHERWISE SPECIFIED USE THE FOLLOWING:--			REV NO. 1	TITLE ASM.	PORT ON 5481	IN 12.1		
APPLIED PRACTICES	SURFACES	TOLERANCES ON MACHINE DIMENSIONS	107C5327	DUMMY FUEL ROD	FIRST MADE FOR FUEL BUNDLE			
145AS481	✓	<table border="1"> <tr> <th>FRACTIONS</th> <th>DECIMALS</th> <th>ANGLES</th> </tr> <tr> <td>+</td> <td>+</td> <td>+</td> </tr> </table>					FRACTIONS	DECIMALS
FRACTIONS	DECIMALS	ANGLES						
+	+	+						
CONT. ON SHEET			SHEET NO. 1

Ⓔ Ⓕ

1. SCRATCHES, NICKS, ETC. INTRODUCED IN THE TUBING FABRICATION & HANDLING SHALL NOT EXCEED .002 IN DEPTH.
2. FILL VOIDS WITH GRAFHE (99.995% PURE) HELIUM ESCAPE THROUGH TUBES & END PLUGS OR WELDED REGIONS. SHALL NOT EXCEED 10^{-8} STD. CM³/SEC. OF HELIUM WITH A VACUUM OF 20 MICRONS OF MERCURY.
3. ALL END PLUGS, TENSILE SPECIMENS, WIRES, AND ROD (PI3) SURFACES SHALL BE FREE OF ALL VOLATILE CONTAMINANTS AT ASSEMBLY.
4. OUTSIDE DIAMETER OF END PLUG WELD SHALL NOT EXCEED .468 INCHES. THICKNESS OF TUBING OR WELD AT WELD ZONE SHALL NOT BE LESS THAN .029 INCHES.

16. TENSILE SPECIMENS MAY BE WIRED AT RANDOM.

[illegible]

Figure 5-2 Details of Zr-Cr and Zircaloy-2 Dummy Rods

rod* and provided a means for non-heat-transfer corrosion to be measured by direct weight gain. The basic design of these dummy rods was as simple as possible to facilitate easy access to tensile and corrosion specimens and provide post-irradiation tube samples for burst testing.

In addition, 12 rods of the same basic design as the reload fuel design except that the fuel was 2.42% enriched, were fabricated to be used as replacement rods. Six of these rods were clad with the Zr-Cr alloy, and six were clad with Zircaloy-2.

5.2 TEST VARIABLES

Although the primary purpose of this experiment was the evaluation of Zr-Cr fuel cladding as a function of exposure, various other variables were incorporated into this experiment to make it more complete. These variables include pre-irradiation condition of cladding and the irradiation environment.

5.2.1 EXPOSURE

The maximum target exposure was 20,000 MWd/TU average burnup. Nine fuel and two dummy rods were removed during the June-July reactor shutdown to obtain post-irradiation data at about 8000 MWd/TU average before the termination of the program. Eleven replacement rods were inserted to reconstitute the bundle. During the April-May, 1969 reactor outage, three additional rods were removed and examined in the fuel pool for information at ~ 14,300 MWd/TU exposure. The irradiation schedule and the various types of fuel and dummy rods for this experiment are shown in Table 5-1.

5.2.2 PRE-IRRADIATION CLADDING CONDITION

Three pre-irradiation cladding conditions were tested:

- As-etched,
- Low temperature autoclaved at 300°C for 60 hours, and
- Standard temperature autoclaved at 400°C for 14 hours.

The testing of these initial cladding conditions was prompted by recent BNWL tests in which it was observed that in-reactor corrosion rates for Zircaloy-2 and Zr-Cr in high pH pressurized water varied considerably with pre-irradiation conditioning. (Ref. 9) Since this variable had not

been systematically tested in actual fuel rod experiments, it was considered equally important in this experiment.

5.2.3 IRRADIATION ENVIRONMENT

The fuel rods were irradiated in Consumers Power Company's Big Rock Point reactor. The BRP reactor is a boiling water reactor operating at 1325 psi and 580°F (305°C). The water contains ~ 200 ppb oxygen and 1 to 2 ppb hydrogen, while the steam contains ~ 25 ppm oxygen and 1 to 2 ppm hydrogen.

Three different environments existed during the irradiation testing:

- Heat transfer in reactor water (fuel cladding),
- Nonheat transfer in reactor water (corrosion samples in vented compartments in dummy rods and the dummy rod cladding itself).
- Nonheat transfer in helium (tensile samples in sealed compartments in dummy rods).

The environments allowed separation of effects, if any, caused by heat transfer during irradiation on corrosion rates and mechanical properties.

5.3 OPERATING HISTORY OF TEST FUEL RODS

To operate the rods run as hot as possible, and to evaluate the Zr-Cr alloy operating at maximum temperatures, the Zr-Cr clad fuel rods, the control Zircaloy-2 clad fuel rods, and the dummy rods were inserted in peripheral locations of Assembly B-1. The irradiation began in June 1967. The rate of fuel burnup was approximately 800 MWd/TU (average) per month of full power. At the end of the third cycle (April 1969) of reactor operation, the initial Zr-Cr clad rods had accumulated an average exposure of approximately 14,300 MWd/TU, with a total time of high-temperature reactor exposure of approximately 14,200 hours. The irradiation is continuing to the target discharge exposure of 20,000 MWd/TU.

5.3.1 INITIAL LOADING PLAN FOR THE TEST FUEL RODS

To evaluate maximum irradiation temperature conditions, the test fuel rods were located in the peripheral positions of Assembly B-1. Figure 5-3 is a schematic showing the initial

* Autoclave tests in high oxygen steam at 300°C (572°F) (20 ppm O₂) showed that tantalum exhibits excellent corrosion resistance at reactor temperatures.

TABLE 5-1
Zr-Cr FUEL IRRADIATION EXPERIMENT

Rod Description

Item	Cladding Alloy	Pre-Irradiation (a) Cladding Condition	Rod Type (b)
1	Zr-Cr Alloy	1	Fuel Rod
2	Zr-Cr Alloy	2	Fuel Rod
3	Zr-Cr Alloy	3	Fuel Rod
4	Zr-Cr Alloy	1, 2, and 3	Unfueled Dummy
5	Zircaloy-2	1	Fuel Rod
6	Zircaloy-2	2	Fuel Rod
7	Zircaloy-2	3	Fuel Rod
8	Zircaloy-2	1, 2, and 3	Unfueled Dummy

Loading Plan

Item	Number of Initial Rods	At 8000 MWd/TU		At ~ 14,300 MWd/TU (d)	
		Removed	Replaced	Removed	Replaced
1	4	2	2	0	0
2	6	2	2	0	0
3	6	2	2	2	*
4	2	1	0	0	0
5	2	1	0	0	0
6	2	1	0	1	*
7	2	1	5	0	0
8	2	1	0	0	0

Fabrication Schedule

Item	Number of Rods to be Fabricated	Identification of 26 Initial Rods	Identification of 12 Replacement Rods
1	4 plus 2 spares	FR4-1 through FR4-4	FR4-21 and FR4-22
2	6 plus 2 spares	FR-4 through FR4-10	FR4-25 and FR4-26
3	6 plus 2 spares	FR-11 through FR4-16	FR4-31 and FR4-32
4	2	DR1-1 and DR1-2	—
5	2	FR2-4 and FR2-5	—
6	2	FR2-6 and FR2-7	—
7	2 plus 6 spares	FR2-8 and FR2-9	FR2-10 through FR2-15
8	2 plus 1 spare	DR2-3 and DR2-4	—

- (a) Zr-Cr alloy and Zircaloy-2 tubing were rocked-to-size and annealed.

Number designation refers to:

- 1—Cladding etched and cleaned;
- 2—Cladding etched, cleaned, and autoclaved at 300°C for 60 hours; and
- 3—Cladding etched, cleaned, and autoclaved at 400°C for 14 hours.

- (b) Initial fuel rods contain 2.6% enriched UO_2 pellets. Replacement rods contain 2.42% enriched UO_2 pellets.

- (c) Completed during June–July 1968 outage.

- (d) Completed during April–May 1969 outage.

* Replaced with irradiated fuel rods from another assembly.

*DENOTES ROD
REMOVED DURING
JUNE-JULY 1968
FUEL OUTAGE

	a	b	c	d	e	f	g	h	i	j	k
1			FR4-1	FR4-5	FR2-6*	DR2-3*		FR2-5*	FR4-11		
2		FR4-9*								FR4-15*	
3	FR4-14*										FR4-2
4	FR2-4										FR4-6
5											
6	DR1-1*										DR4-2
7											
8	FR4-8*										FR2-9
9	FR4-4*										FR4-12
10		FR4-16								FR4-10	
11			FR4-13	FR2-9		DR2-4	FR2-8*	FR4-7	FR4-3*		

← ORIENTATION
HOLE

GEAP-10044

Figure 5-3 Location of Test Fuel and Dummy Rods in Assembly B-1 at Start of Irradiation Program, June 1967

rod locations in the assembly. Table 5-2 lists the rods, their surface pretreatment, and their average relative power factors. The Zr-Cr clad rods have been placed in the hottest peripheral positions in the assembly.

5.3.2 FIRST AND SECOND CYCLES (JUNE 1967 – JUNE 1968)

The first cycle of the irradiation program ran from June 14, 1967, to February 11, 1968. The second cycle ran from March 15, 1968, to June 21, 1968. At the end of the second cycle, Assembly B-1 had accumulated approximately 8000 MWd/TU average exposure. This corresponds to 7900 hours of high-temperature, full-power reactor operation.

During the first and second cycles of the irradiation program, Assembly B-1 ran as one of the hottest assemblies in the core. With the reactor operating at full power, the hottest Zr-Cr clad rods operated with a peak heat flux of approximately 320,000 Btu/h-ft². Figure 5-4 is a histogram showing the operating power of the Big Rock Point Reactor for the two cycles. During the June–July 1968 reactor outage, the assembly was examined in detail in the reactor pool. (See Section 5 for the results of the pool examination).

At the end of Cycle 2 (June–July, 1968 reactor outage), the first group of test fuel rods and dummy rods were removed from the assembly. Six Zr-Cr rods, three Zircaloy-2 clad fuel rods, and two dummy rods were removed, and the bundle was reconstituted with the replacement rods and returned to the core to continue the irradiation program. Table 5-2 lists the rods removed and the replacement rods. The total time of high-temperature reactor exposure of the rods removed was approximately 7900 hours. Using an underwater shear in the reactor pool, the nine fuel rods were cut in half and returned to Vallecitos Nuclear Center in a 700-EX series cask for the post-irradiation examination. (See Section 6 for the results of this examination.) The dummy rods were returned as full-length rods in another cask.

5.3.3 THIRD CYCLE (JULY 1968 – APRIL 1969)

The third cycle of test rod irradiation ran from July 15, 1968, to April 19, 1969. A histogram of the reactor power is shown in Figure 5-4. Assembly B-1 was at times the hottest bundle in the core. The peak heat flux in the hottest Zr-Cr rod reached ~337,000 Btu/h-ft² at full-power reactor operation. As of April 19, 1969, the assembly had accumulated, since the start of the irradiation program, ~14,300 MWd/TU (13,800 hours at temperature). The rods inserted during the June–July 1968 reactor outage

had accumulated ~ 6,300 MWd/TU (5900 hours at temperature).

During the April–May 1969 outage, three test rods were removed from the assembly. Table 5-2 lists the rods removed. The bundle was reconstituted with rods from another irradiated assembly. A detailed account of the pool examination of the assembly during the reactor outage at the end of the third cycle is given in subsection 5.4 of this report.

5.3.4 FOURTH CYCLE (MAY 1969 – FEBRUARY 1970)

The fourth cycle started on May 12, 1969, and is scheduled to continue to February 1970. By the end of the cycle, the Zr-Cr clad rods will have reached their target discharge exposure of 20,000 MWd/TU (12,000 MWd/TU exposure for the rods inserted in June 1968).

5.4 SITE INSPECTION

Assembly B-1 is the carrier assembly for the Zr-Cr clad test fuel rods. The assembly has been leak-checked and visually examined during each of the three reactor outages. A summary of the site inspections is presented.

5.4.1 INSPECTION OF ASSEMBLY B-1 DURING FEBRUARY 1968 OUTAGE

Assembly B-1 was the highest power assembly in the Big Rock core during this run. The assembly was leak-checked and found to be sound, with no indication of failures. A visual examination was performed, using a periscope. All four sides of the assembly were examined. The most obvious feature in the assembly was that the dummy rods had no scale deposits and exhibited a mat black finish. All of the power-producing rods in the assembly showed a reddish scale deposit typical of all fuel assemblies examined. There were no differences in appearance between the power-producing rods; that is, the different alloys – Zircaloy-2 and Zr-Cr – and the different pre-conditionings – etched, 300°C autoclaved, or 400°C autoclaved – made no difference in the appearance of the rods.

The top third of the fuel rod surfaces had little deposits, and had the same appearance as the dummy rods – a dull, black finish. Both the bottom and the top end plugs were examined in detail. There were no indications of any anomalies and no particular differences in the appearance of the weld heat-affected zone near the end plugs. On the dummy rods, it was possible to see some difference in color at the welds that joined the various sections together. The heat-affected zones were slightly lighter in color. The

Table 5-2
 ROD LOCATIONS FOR Zr-Cr ALLOY EXPERIMENT IN B-1 BUNDLE

Number	B-1 Assembly Location	Relative Rod Power	Cladding Alloy	Cladding Condition	Removed June 1968	Replaced With	Cladding Alloy	Cladding Condition	Removed April 1969
<i>Fuel Rods</i>									
FR2-4	a-4	1.14	Zirc-2	1	—	—	—	—	—
FR2-5	b-1	1.14	Zirc-2	1	FR2-5	FR2-10	Zirc-2	3	—
FR2-6	e-1	1.10	Zirc-2	2	FR2-6	FR2-11	Zirc-2	3	—
FR2-7	k-8	1.14	Zirc-2	2	—	—	—	—	—
FR2-8	g-11	1.10	Zirc-2	3	FR2-8	FR2-12	Zirc-2	3	—
FR2-9	d-11	1.14	Zirc-2	3	—	—	—	—	FR2-9
FR4-1	c-1	1.22	Zr-Cr	1	—	—	—	—	—
FR4-2	k-3	1.22	Zr-Cr	1	—	—	—	—	—
FR4-3	i-11	1.22	Zr-Cr	1	FR4-3	FR4-21	Zr-Cr	1	—
FR4-4	a-9	1.22	Zr-Cr	1	FR4-4	FR4-22	Zr-Cr	1	—
FR4-5	d-1	1.14	Zr-Cr	2	—	—	—	—	—
FR4-6	k-4	1.14	Zr-Cr	2	—	—	—	—	—
FR4-7	h-11	1.14	Zr-Cr	2	—	—	—	—	FR4-7
FR4-8	a-8	1.14	Zr-Cr	2	—	FR4-25	Zr-Cr	2	—
FR4-9	b-2	1.16	Zr-Cr	2	FR4-8	FR4-26	Zr-Cr	2	—
FR4-10	j-10	1.16	Zr-Cr	2	FR4-9	—	Zr-Cr	—	—
FR4-11	i-1	1.22	Zr-Cr	3	—	—	—	—	—
FR4-12	k-9	1.22	Zr-Cr	3	—	—	—	—	—
FR4-13	c-11	1.22	Zr-Cr	3	—	—	—	—	FR4-13
FR4-14	a-3	1.22	Zr-Cr	3	FR4-14	FR4-31	Zr-Cr	3	—
FR4-15	j-2	1.16	Zr-Cr	3	FR4-15	FR4-32	Zr-Cr	3	—
FR4-16	B-10	1.16	Zr-Cr	3	—	—	—	—	—
<i>Dummy Rods</i>									
DR2-3	i-1	0	Zirc-2	1,2, and 3	DR2-3	FR2-13	Zirc-2	3	—
DR2-4	f-11	0	Zirc-2	1,2, and 3	—	—	—	—	—
DR4-1	a-6	0	Zr-Cr	1,2, and 3	DR4-1	FR2-14	Zr-Cr	3	—
DR4-2	k-6	0	Zr-Cr	1,2, and 3	—	—	—	—	—

* Zr-Cr alloy and Zircaloy-2 tubing were rocked to size and annealed.
 Number designation refers to:
 1 — Cladding etched and cleaned;
 2 — Cladding etched, cleaned, and autoclaved at 300°C for 60 hours; and
 3 — Cladding etched, cleaned, and autoclaved at 400°C for 14 hours.

FIGURE 5-4. REACTOR POWER HISTOGRAM —
CONSUMERS BIG ROCK POINT
REACTOR — Zr-Cr IRRADIATION
PROGRAM

dummy sections have segments which have holes in them to allow water ingress for corrosion tests. These open holes appeared clear and sharp at the edges. It was possible to see into the rod through the holes. The edges of the corrosion and tensile specimens could be seen within the dummy rods.

Near the second spacer from the bottom, the scale deposit was fairly light and scale deposition outlining the position of each pellet interface in the fuel column stack could be seen. Selected rods were removed from bundle B-1 and were profiled. The profiles showed no unusual characteristics, and were similar to profiles of other rods obtained during the shutdown. Assembly B-1 was returned to the core and all of the Zr-Cr alloy clad fuel rods continued to be irradiated.

5.4.2 INSPECTION OF ASSEMBLY B-1 DURING JUNE-JULY 1968 OUTAGE

Assembly B-1 was removed from the core. The assembly was leak-checked and found to be sound. All four sides of the assembly were visually examined. The visual examination indicated no basic change in the surface appearance of the Zr-Cr or Zircaloy-2 clad rods since the February 1968 examination. There are no differences in appearance between the power-producing rods — the different alloys, Zircaloy-2 and Zr-Cr — and the different preconditionings — etched, 300°C autoclaved, or 400°C autoclaved. It was apparent that additional scale had deposited on the fuel rods.

Nine fuel rods (six Zr-Cr clad rods and three Zircaloy-2 clad rods) were removed from the assembly. The assembly was reconstituted with the replacement rods and returned to the core to continue the irradiation program.

5.4.3 INSPECTION OF ASSEMBLY B-1 DURING THE APRIL - MAY 1969 OUTAGE

This last cycle (July 1968 to April 1969) has provided an unexpected, stringent test of the primary performance advantage of the Zr-Cr alloy; i.e., its improved corrosion resistance at elevated temperatures. Under similar local over-temperature conditions caused by higher than expected scale deposition, a Zircaloy-2 clad rod failed, while the Zr-Cr clad rods survived. Although the results are hardly conclusive, they do tend to confirm the superior corrosion resistance of the Zr-Cr alloy. A detailed account of the examination is provided in the following paragraphs.

During part of the last cycle, the assembly operated as the hottest "B" assembly in the core. During the outage the

assembly was removed from the core and leak checked. Leak checking indicated the presence of a rod failure within the assembly.

A visual examination of all four sides of the assembly revealed two rods as suspect failures. Scale spalling was noted on one Zircaloy-2 clad rod (position 11-e) and one Zr-Cr clad rod (FR4-7) (position 11-h). The Zircaloy-2 rod was one of the original standard rods in the assembly. The Zr-Cr clad rod was one of the initial rods inserted into the assembly as part of the Zr-Cr irradiation program. Both types of rods had been irradiated since June 1967 and had accumulated a bundle average exposure of ~ 14,300 MWd/TU.

All 16 Zr-Cr clad rods were removed from the bundle and leak-checked separately. The leak check indicated that all of the Zr-Cr clad rods were sound. With the suspect Zircaloy-2 clad rod removed and the Zr-Cr clad rods removed, the assembly was re-leak-checked. This leak check indicated that the remaining rods in the assembly were sound. The one Zr-2 clad rod was apparently the only failed rod in the assembly.

A thorough visual examination was performed on the Zr-Cr clad rod. Figure 5-5 shows the surface scale spalling on the rod. The spalling occurred just above the center spacer location and proceeded upward for ~ 7 inches. The rod was removed from the assembly and profiled. Except in the area of the scale spalling, the profile trace had no unusual characteristics and was similar to traces of other rods obtained during the shutdown. As would be expected in the area of the scale spalling, the profile trace was quite erratic. However, no indications of the rod bulging or cladding penetration were found on the profile trace.

During profilometry, the loose scale was chipped away, revealing areas of white corrosion. (See Figure 5-5). One locally attacked area appeared to have been corroded ~ 0.010 inch into the wall. The corrosion attack along the rest of the rod appeared to be more general.

The post-irradiation examinations of the Zr-Cr clad rods and control Zircaloy-2 rods removed from Assembly B-1 during the June-July 1968 outage revealed post-transition corrosion at the spacer positions on both the Zr-Cr clad rods and the Zircaloy-2 clad rods. The Zr-Cr clad rods were unique in that the corrosion attack was localized, resulting in a "pimply" appearance. These pimples could be seen before the scale was removed.

AREA OF LOCALIZED CORROSION
~ 0.010 in. DEEP

Figure 5-5 Zr-Cr Clad Rod FR4-7, Irradiated Since June 1967.
Assembly Average Exposure of 14,300 MWd/TU,
Total Time at Temperature ~13,800 Hours.

Figure 5-6 Middle-Intermediate Spacer Location on Rod FR4-7.

Figure 5-6 shows the appearance of the center spacer position of the Zr-Cr clad rod (FR4-7). With one additional cycle of exposure, the "pimply" appearance is apparent; however, the corrosion attack appears to have advanced considerably.

The Zr-Cr clad rod (FR4-7) was removed from the bundle, along with one other Zr-Cr (FR4-13) and another Zircaloy-2 (FR2-9) rod with comparable burnup. Assembly B-1 was reconstituted with irradiated rods from another assembly and returned to the core.

5.4.4 Bundle B-1 Failure Interpretation

The general buildup of crud and scale on Bundle B-1 during the two cycles of operation since March 1968 has significantly exceeded previous experience and the limits considered in the original design. This same condition has been observed with other fuel in the BRP core, during the same time period. The deposit accumulation does not appear to be a direct function of relative bundle power or heat flux in contrast to the previous patterns measured on the fuel rods after earlier operating cycles. Previously, the deposition was thinner and the deposition pattern more closely followed the rod axial power distribution. The composition of the most recent scale in all cases is predominantly copper oxide, a historically troublesome and unpredictable impurity in terms of behavior. (Understanding of these unfavorable characteristics has led to stringent limits on feedwater introduced impurities, particularly copper, in modern BWR designs, along with appropriate feedwater system materials selection and condensate demineralizer equipment design to control to these limits.)

At the conclusion of the last BRP cycle, other failed fuel bundles were observed in addition to Bundle B-1. Although differing in minor details, the general condition of all the failed rods examined was substantially identical to the B-1 rod failure, and there was a strong correlation between failure and high heat rating. On the basis of these observations, it has been tentatively concluded that all of the failures, including the B-1 bundle, were caused by cladding overheating and consequent accelerated corrosion at peak power locations, leading ultimately to through-wall penetrations. Heavy crud deposition appears to be the prime contributor to the cladding overtemperature. Corrosion calculations taking into account the observed deposits and fuel operating parameters support this failure interpretation. It should be recognized that this failure interpretation is based exclusively on information developed at the reactor site examination during the outage. No hot-cell examinations have been performed.

The BRP reactor went back on the line on May 5, 1969, and continues to operate satisfactorily. However, it is clear that the excessive crud deposition rate must be corrected before the centermelt fuel irradiations can be resumed.

6. POST-IRRADIATION EXAMINATION

Nine fuel rods and two dummy rods were removed from the B-1 assembly during the June-July 1968 outage. The assembly had accumulated ~ 8000 MWd/TU (total time of high temperature reactor exposure was 7900 hours). The

rods were returned to the Vallecitos Nuclear Center for post-irradiation evaluation. Table 6-1 lists the rods returned, their average exposure, and the work scope of the post-irradiation examination.

TABLE 5-1
SCOPE OF POST-IRRADIATION EXAMINATIONS, Zr-Cr ALLOY DEVELOPMENT

Rods Removed from Assembly B-1 After ~ 8,000 MWd/TU Average Burnup (7,900 h)

B-1 Assembly Position	Rod Serial No.	Cladding Alloy	Initial Cladding Surface Condition	Rod Contents	Enrich- ment	Relative Rod Power	Avg. Rod Burnup MUd/TU	POST-IRRADIATION WORK						
								Visual	γ Scan	Profile	Remove Crud	Repeat Profile	Repeat Visual	Cut Samples
h-1	FR2-5	Zr-2	.1	UO ₂	2.6%	1.14	9120	Yes	---	---	Yes	---	Yes	Yes
c-1	FR2-6	Zr-2	2	UO ₂	2.6%	1.10	8800	Yes	---	---	Yes	---	Yes	Yes
g-1	FR2-8	Zr-2	3	UO ₂	2.6%	1.10	8800	Yes	---	---	Yes	---	Yes	Yes
i-11	FR4-3	Zr-Cr	1	UO ₂	2.6%	1.22	9760	Yes	Yes	---	---	---	---	?
a-9	FR4-4	Zr-Cr	1	UO ₂	2.6%	1.22	9760	Yes	Yes	Yes	Yes	Yes	Yes	Yes
b-2	FR4-9	Zr-Cr	2	UO ₂	2.6%	1.14	9120	Yes	Yes	---	---	---	---	?
a-8	FR4-8	Zr-Cr	2	UO ₂	2.6%	1.15	9280	Yes	Yes	Yes	Yes	Yes	Yes	Yes
j-2	FR4-15	Zr-Cr	3	UO ₂	2.6%	1.22	9760	Yes	---	---	---	---	---	?
a-3	FR4-14	Zr-Cr	3	UO ₂	2.6%	1.15	9280	Yes	Yes	Yes	Yes	Yes	Yes	Yes
F-1	DR2-3	Zr-2	1,2,3	Samples	—	—	—	Visual Yes			Remove Samples Yes		Cut Samples Yes	
a-3	DR4-1	Zr-Cr	1,2,3	Samples	—	—	—	Yes			Yes		Yes	

Initial Surface Conditions:

1. Etched and Cleaned (0 mg/dm²)
2. Etched, cleaned, and autoclaved 300°C for 60 h (2.6 mg/dm²)
3. Etched, cleaned, and autoclaved 400°C for 14 h (5.9 mg/dm²)

6.1 VISUAL EXAMINATION (BEFORE SCALE REMOVAL)

The surfaces of the rods had a reddish-brown color typical of system corrosion product scales. At the top and bottom of the rods, the black oxide (ZrO_2) could be seen through the thin scale deposit. There were no indications of any anomalies or any particular difference between the end plug weld heat-affected zones and the areas away from the heat-affected zones on any of the rods.

Relatively thick scale deposits were found at spring contact areas at the intermediate spacer positions. Figure 6-1 shows typical scale deposition at the spacer location of rod FR4-8. "Pimple"-like protuberances were found on all of the Zr-Cr clad rods in the area of the intermediate spacer locations. These formations were most prominent at the lower intermediate spacer location. Evidence of these formations was found only at the spacer locations of the Zr-Cr clad rods.

Superficial scale spalling or evidence of the scale beginning to spall was found on rods FR4-3, FR4-4, FR4-9, and FR4-14. The scale spalling occurred in areas of relatively thick scale deposition just above or below the middle intermediate spacer position. The most pronounced area of spalling occurred on rod FR4-14 just above the middle intermediate spacer position, and is shown in Figure 6-2.

6.2 GAMMA SCANS

Rods FR4-3, FR4-4, FR4-8, FR4-9, and FR4-14 were gamma-scanned. Figure 6-3 shows the gamma scan of rod FR4-14 (one of the highest powered rods), and it is typical of the gamma scans of the other four rods. The peak power position in all of the rods occurred just above the middle intermediate spacer positions. Note the depressions on the gamma scan at the axial positions corresponding to the spacer locations.

6.3 PROFILOMETRY (BEFORE AND AFTER SCALE REMOVAL)

Full-length dimensional profiles (longitudinal traverse with rotation), before scale removal, were performed on rods FR4-4, FR4-8, and FR4-14. The dimensional profile of rod FR4-14 is shown in Figure 6-4 and is typical of the profiles of the other two rods. The most prominent feature of the profiles are the sharp diameter increases at the spacer locations caused by localized scale buildups. The scale deposition apparently has caused an increase in the diameter of the center portion of the rod. Note that at the spacer locations, the low point of the profiles is approximately the same diameter as the ends of the rod. Considerable ovality was found in the areas of high scale

deposition. In the areas of the scale spalling, the sharp jogs in the profile trace indicate that the spalling is superficial and is only about 50μ (0.002 inch) deep.

The sheared ends and fission gas puncture holes on rods FR2-5, FR2-6, FR2-8, FR4-4, FR4-8, and FR4-14 were filled with epoxy, and the rods were soaked in hot HCl to remove the scale. After removal of the scale, rods FR4-4, FR4-8, and FR4-14 were reprofiled. Figure 6-5 is the profile of rod FR4-14 after scale removal and is typical of all of the profiled rods. The spurious peaks were caused by epoxy or dirt on the surface of the rod. There is more ovality in the center region of the rod than there is at the ends of the rod. At the lower intermediate spacer location there is an apparent slight increase in the diameter of the rod. The profiles appeared as expected, with no indications of bulging or impending failure.

By comparing the profiles made before and after scale removal, the scale thickness was estimated to range from zero at the top and bottom end plugs, to a maximum just above or just below the middle-intermediate spacer location. The thickest, most uniform scale deposits were found to be located just below the middle-intermediate spacer locations. The scale thickness on the diameter just below the middle-intermediate spacer locations on rods FR4-4, FR4-8, and FR4-14 was ~ 150 , 102 , and 135μ respectively.

6.4 VISUAL EXAMINATION (AFTER SCALE REMOVAL)

The scale was removed from three Zr-Cr and three Zr-2 clad rods. These rods were then thoroughly examined. Outside of the spacer locations, both the Zr-Cr and Zircaloy-2 clad rods had black lustrous adherent oxide (ZrO_2) films, with no indications of post-transition corrosion. Figure 6-6 shows surface appearance of the Zr-Cr clad rods in the area of highest heat flux just above the middle-intermediate spacer position. The Zr-Cr clad rods were comparable to the Zr-2 clad rods. No particular difference in surface appearance could be seen between the rods with different initial surface pretreatments.

The end plug welds on the rods were examined in detail. It was possible to see some difference in surface color at the welds on all of the rods. The heat-affected zones were slightly lighter in color on both the Zircaloy-2 rods and the Zr-Cr rods. The Zircaloy-2 and Zr-Cr clad rods were comparable in color at the top end plug welds. The Zr-Cr clad rods were darker in color at the bottom weld heat-affected zone than the Zircaloy-2 clad rods. This effect is shown in Figure 6-7. No obvious difference was noted in the color of the weld heat-affected zone of the rods with different surface preparations.

NOTE: "PIMPLE-LIKE" PROTUBERANCES IN THE AREA OF THE SPACER LOCATION THE OBLONG SHAPES ARE THE SPACER SPRING CONTACT AREAS. NOTE THAT THE CRUD HAS SPALLED OFF AT ONE OF THE SPACER SPRING CONTACT AREAS AND THE TUBING WALL CAN BE SEEN IN THE SPALL AREA.

Figure 6-1 View of Spacer Spring Contacts at Lower Intermediate Spacer Location on Rod FR4-8

NOTE: THE SPIRAL LINES ARE FROM THE DIMENSIONAL PROFILE TRACE.

Figure 6-2 Superficial Scale Spalling on Rod FR4-14

Both the Zr-Cr clad rods and the Zircaloy-2 clad rods exhibited white oxide at the spacer locations. The Zircaloy-2 clad rods exhibited a patch-like area of white oxide at the spacer spring contact areas. The Zr-Cr clad rods had similar, but smaller, patches at the spacer spring contact areas. The Zr-Cr clad rods exhibited small areas of localized corrosion surrounding the spacer spring contact

points. These small areas of localized corrosion apparently caused the "pimply" effect seen in the initial visual examination (before scale removal). Also, the slight increase in diameter found in the profiles of the Zr-Cr rods at the lower intermediate spacer location is apparently caused by the oxide buildup.

Figure 6-3 Gamma Scan of Rod FR4-14

Figure 6-4 Dimensional Profile of Rod FR4-14 Before Removal of Scale

Figure 6-5 Dimensional Profile of Rod FR4-14 After Removal of Scale

Figure 6-6 Surface Appearance of Zr-Cr Clad Rods in Highest Heat Flux Area

BOTTOM END PLUG

TOP END PLUG

Zr-2
FR2-5
AS ETCHED

BOTTOM END PLUG

TOP END PLUG

Zr-Cr
FR4-4
AS ETCHED

Figure 6-7 Photographs of Bottom and Top End Plug Welds on Rods FR2-5 and FR4-4

Figures 6-8, 6-9, and 6-10 show the lower and upper intermediate spacer locations of the Zr-Cr clad and the Zircaloy-2 clad rods. The Zr-Cr clad rods appear to have more white corrosion products at the lower intermediate spacer position than at the upper intermediate spacer position. In contrast, the Zircaloy-2 clad rods exhibited less white corrosion products at the lower intermediate spacer position than at the upper intermediate spacer position. Also, qualitatively, it appears that the as-etched surface pretreatment rods exhibit less corrosion at the spacer locations than the 400°C autoclaved rods for both the Zr-Cr alloy and the Zircaloy-2 alloy. The severity of the corrosion at the middle-intermediate spacer location appeared to be between the two extremes of the corrosion at the upper and lower intermediate spacer locations. No evidence of white oxide was observed at either the upper or lower spacer location on both the Zr-Cr clad rods or the Zircaloy-2 clad rods. The upper spacer location was in the area of the plenum region, and there is no heat flux in this area. The lower spacer location has minimal heat flux in that area.

The white oxide appeared to be unique to the spacer locations for both the Zircaloy-2 alloy and the Zr-Cr alloy. Outside of the spacer locations both alloys appeared to have excellent corrosion performance.

6.5 METALLOGRAPHIC EXAMINATIONS

6.5.1 DUMMY ROD CLADDING

The two dummy rods (one clad with Zr-Cr tubing and one clad with Zircaloy-2 tubing) are nonfueled rods containing tensile specimens. The rods were exposed under isothermal conditions in the same environment and for the same period of time as the fuel rods. The rods are compartmented; each compartment is clad with tubing with one of the three cladding surface pre-treatments.

Three transverse sections were prepared from the cladding of each of the dummy rods. Each of the three sections were from cladding of one of the three different surface pre-treatments. Figure 6-11 is a schematic of the dummy rods, showing the location from which sections were taken and the initial surface pre-treatment of the cladding.

Photomicrographs of the oxide films from representative areas of the sections are shown in Figure 6-12. All specimens appeared to have relatively uniform oxide films; however, the Zr-Cr specimens appear to have a more dense and a more uniform oxide film than the Zircaloy-2 specimens have. Note the jagged nature of the metal-oxide interface on the Zircaloy-2 specimens compared to the

relatively smooth metal-oxide interface of the Zr-Cr specimens.

The thickness of each of the oxide films was measured, and the thickness measurements were converted to weight gains. The weight gain results of the Zircaloy-2 and Zr-Cr specimens are compared in Table 6-3. The weight gains of the Zircaloy-2 specimens are higher than the Zr-Cr specimens with the same surface pre-treatment. After the 7900 hours of exposure, the Zircaloy-2 weight gains appear to be a function of surface pretreatment, with the as-etched having the lowest weight gain and increasing weight gains corresponding to higher temperature autoclave treatments. The Zr-Cr specimens do not show the same correlation between weight gain and the surface pretreatment. Since the specimens from the same rod were taken from different axial positions, the weight gains between specimens in the same rod may be affected by exposures to different steam qualities and neutron fluence.

Microhardness measurements were taken on a Zr-Cr specimen and a Zircaloy-2 specimen. The specimens were from the same axial position of each rod, and were in the area of peak neutron fluence. The hardnesses are tabulated as follows:

	No. of Indentations	Average Hardness DPH
Zr-Cr	5	214
Zr-2	5	207

The hydrogen level has been estimated from the hydride content in the metallographic sections to be well below 50 ppm in all of the specimens. No evidence of gross hydriding was found in any of the specimens.

6.5.2 FUEL ROD CLADDING

Transverse metallographic sections have been prepared from selected areas of rods FR2-5, FR2-6, FR2-8, FR4-4, FR4-8, and FR4-14. The sections from rods FR2-5, FR2-6, FR4-4, and FR4-8 were taken ~ 1 inch below the middle intermediate spacer location. This area was the area of thickest uniform scale deposition. The sections from rods FR2-8 and FR4-14 were taken through the spacer spring contact area in the middle intermediate spacer location.

Metallographic examination of the sections from rods FR2-5, FR2-6, FR4-4, and FR4-8 revealed a uniform oxide film completely around the circumference of the rods. Rods FR2-8 and FR4-14 had relatively uniform oxide films away from the spacer spring contact areas. Figure 6-13

TABLE 6-2
OXIDE FILM THICKNESSES AND WEIGHT GAINS OF
IRRADIATED FUEL AND DUMMY RODS

Surface Pretreatment	DUMMY ROD CLADDING				Fuel Rod No.	FUEL ROD CLADDING				
	Zircaloy-2 Oxide Film Thickness (μ)	Weight Gain (Mg/dm ²)	Zr-Cr Oxide Film Thickness (μ)	Weight Gain (Mg/dm ²)		Zircaloy-2 Oxide Film Thickness (μ)	Weight Gain (Mg/dm ²)	Fuel Rod No.	Zr-Cr Oxide Film Thickness (μ)	Weight Gain (mg/dm ²)
Etched and NaOH Cleaned.	4.4	69	4.0	62	FR2-5	3.7	58	FR4-4	2.7	42
Etched, NaOH cleaned, and preoxidized at 300°C for 60 hours	4.9	76	4.1	64	FR2-6	2.5	39	FR4-8	3.1	48
Etched, NaOH cleaned, and preoxidized at 400°C for 12 hours	5.0	78	3.6	56	FR2-8	4.3	67	FR4-14	3.4	53
	—	—	—	—	(Uniform)			(Uniform)		145
					FR2-8		126	FR4-14		
					(Total Avg)	8.1		(Total Avg)	9.3

LOWER-INTERMEDIATE SPACER LOCATION

UPPER-INTERMEDIATE SPACER LOCATION

FR4-4
Zr-Cr
AS ETCHED

LOWER-INTERMEDIATE SPACER LOCATION

UPPER-INTERMEDIATE SPACER LOCATION

FR2-5
ZR-2
AS ETCHED

Figure 6-8 Photographs of Spacer Locations on Rods FR2-5 and FR4-4

LOWER-INTERMEDIATE SPACER LOCATION

UPPER-INTERMEDIATE SPACER LOCATION

FR4-8
Zr-Cr
300°C PREOXIDIZED

LOWER-INTERMEDIATE SPACER LOCATION

UPPER-INTERMEDIATE SPACER LOCATION

FR2-6
Zr-2
300°C PREOXIDIZED

Figure 6-9 Photographs of Spacer Locations on Rods FR2-6 and FR4-8

LOWER-INTERMEDIATE SPACER LOCATION

UPPER-INTERMEDIATE SPACER LOCATION

FR4-14
Zr-Cr
400°C
PREOXIDATION

LOWER-INTERMEDIATE SPACER LOCATION

UPPER-INTERMEDIATE SPACER LOCATION

FR2-8
Zr-2
400°C
PREOXIDATION

Figure 6-10 Photographs of Spacer Locations on Rods FR2-8 and FR4-14

Figure 6-11 Location of Metallographic Sections from Dummy Rods

Figure 6-12 Sections Showing Representative Oxide Films on Dummy Rod Cladding

Figure 6-13 Sections Showing Representative Oxide Films on Fuel Rod Cladding

shows the uniform oxide films from representative areas of these sections. The Zr-Cr oxide films, as also seen on the dummy rod sections, were more dense and uniform than the Zircaloy-2 oxide films. Again, note the jagged nature of the oxide-metal interface on the Zircaloy-2 sections.

The uniform oxide film thicknesses were measured, and the thicknesses were converted to weight gains. The weight gain results of the Zr-Cr specimens and the Zircaloy-2 specimens are compared in Table 6-3. Except for rod FR2-6 which seems to be inconsistent with the rest of the results, the Zr-Cr alloy has slightly better corrosion behavior than the Zircaloy-2 alloy. It should be remembered that all of the Zr-Cr clad rods ran hotter (higher heat flux) than the Zircaloy-2 rods. It is especially interesting to note that the isothermal (dummy rod) specimens for both the Zircaloy-2 alloy and the Zr-Cr alloy had higher weight gains than the fuel rod specimens.

Hydrogen levels estimated from the metallographic sections are below 50 ppm for all of the specimens. No evidence of gross or unusual hydride precipitation was noted in any of the specimens.

Relatively thick oxide films were found at the spacer spring contact areas on rods FR2-8 and FR4-14. Shown in Figure 6-14 is the location of the sections from the rods and the oxide films at the spacer spring contact areas. The thickest oxide film at the spacer spring contact point on the Zircaloy-2 specimen was $\sim 25\mu$ thick. The thickest oxide film at the spacer spring contact point on the Zr-Cr clad rod was $\sim 125\mu$ thick. The thick Zr-2 oxide film was cracked and appeared quite porous. The oxide film on the Zr-Cr specimens appears not to have begun cracking until the oxide film was quite thick. Away from the cracks, the Zr-Cr film appears much denser than the Zircaloy-2 film. Also shown in Figure 6-14 is oxide film through the typical areas of localized corrosive attack ("pimples") on the Zr-Cr rod, away from the spacer spring area. The thickest "pimple" film was $\sim 62\mu$ thick. No concentration of hydride precipitates were found in the areas of thick oxide films on either the Zircaloy-2 or Zr-Cr alloy specimens.

The area of each patch of oxide film was measured and added to the area of the uniform oxide film. The total area was averaged to obtain a total average oxide thickness and weight gain. The results for both the Zr-Cr specimen and Zircaloy-2 specimen are included in Table 6-3. Since these measurements were taken only on one plane through the spacer location, care should be taken in placing too much emphasis on the results.

Microhardness traverses were performed on all of the specimens and are presented in Table 6-4. It is felt

indentations Nos. 1 and 5 were influenced by being too close to the edge of the wall of the cladding; therefore, an average hardness was calculated from the three middle indentations. It is interesting to note that the hardness in the area of the spacer spring contact point was less than the hardnesses away from this area.

6.6 WEIGHT GAIN RESULTS ON CORROSION COUPONS IN DUMMY ROD

Four compartments in each dummy rod were vented by holes in the cladding to allow reactor water to come in contact with the specimens inside. Corrosion coupons machined from the Zr-Cr and Zircaloy-2 tubing were weighed and placed inside the compartments. The primary purposes of the test were to measure direct weight gains on in-pile isothermal (nonheat-transfer) specimens, and to compare the weight gains of the Zr-Cr alloy with the Zircaloy-2 alloy. In addition, to separate the effects of surface pretreatments and make the test more complete, the coupons were prepared with three different initial surface pretreatments.

The corrosion coupons were removed from one of the compartments of each dummy rod and were descaled in a hot (80°C) 50% solution of hydrochloric acid for 16 hours. Each specimen was rinsed in water, rinsed in acetone, dried, and weighed four times. The specimens were then descaled again in hot hydrochloric acid for 16 hours, rinsed in water and acetone, dried, and reweighed four times.

The results of the weighing and the calculated weight gains for each specimen are presented in Table 6-2. The weights of the specimens after the first and second descaling operations agreed quite well (except for specimen Z2-16), indicating that all of the scale had been removed. Visual examination confirmed this.

The weight gain for the Zircaloy-2 specimens is reasonable and somewhat consistent with the weight gain results on the dummy rod cladding (see subsection 6.5.1). However, with the as-etched specimen having a higher weight gain than the 400°C preoxidized specimen, the effect of the surface pre-treatment on the weight gain is opposite of what would be expected.

The weight gains on the Zr-Cr alloy coupons were inconsistent among themselves, and with the weight gain results on the dummy rod cladding specimens. It is felt that the environment inside the dummy rod was considerably different from the environment directly outside the rod. Some evidence to substantiate this conclusion was that the weight gain on the "B" specimens were consistently higher than the weight gain of the "A" specimens. The "A" and "B" specimens with the same surface initial pre-treatment

TABLE 6-3
WEIGHT GAIN RESULT ON CORROSION COUPONS
FROM DUMMY RODS

Specimen Description	Sample No.	Weight After First Descale (gm)	Weight After Second Descale (gm)	Average Weight (gm)	Original Weight (gm)	Weight Gain (gm)	Weight Gain (mg/dm ²)
<i>Zr-Cr</i>							
As Etched	V1-A	3.1641	3.1642	3.1642	3.1553	0.0089	76
	V1-B	3.1914	3.1921	3.1918	3.1673	0.0245	211
300° Preoxidation For 60 hours	V2-A	3.1200	3.1201	3.1200	3.1124	0.0076	66
	V2-B	3.3138	3.3137	3.3138	3.2822	0.0316	272
400° Preoxidation For 14 hours	V3-A	3.3727	3.3714	3.3720	3.3582	0.0138	118
	V3-B	3.1972	3.1973	3.1972	3.1732	0.0240	207
<i>Zircaloy-2</i>							
As Etched	Z1-A	2.6842	2.6841	2.6842	2.6757	0.0085	73
	Z1-B	2.8378	2.8378	2.8378	2.8290	0.0088	76
300° Preoxidation For 60 hours	Z2-A	2.8484	2.8484	2.8484	2.8405	0.0079	68
	Z2-B*	(2.7826)*	2.7866*	2.7866*	0.0079	66*	
400° Peroxidation For 14 hours	Z3-A	2.9159	2.9159	2.9159	2.9089	0.0070	60
	Z3-B	2.961	2.9261	2.9261	2.9183	0.0078	67

* Sample weight after first descale is not consistent with weight after second descale.
Weight after second descale has been used to calculate weight gain.

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TABLE 6-4
DIAMOND PYRAMID HARNESS TRAVERSES ON
TRANSVERSE SECTIONS OF FUEL ROD CLADDING

	Ident. No.	Zircaloy-2 FR2-5	Zircaloy-2 FR2-6	Rod No.	
				Zircaloy-2 (a) FR2-8	Zircaloy-2 (b) FR2-8
O.D.	1	205	191	210	203
	2	217	212	219	212
	3	205	219	227	212
	4	210	217	219	212
I.D.	5	195	217	212	199
Avg (2,3, & 4)		211	216	222	212
	Ident. No.	Zr-Cr FR4-4	Zr-Cr FR4-8	Rod No.	
				Zr-Cr (a) FR4-14	Zr-Cr (b) FR4-14
	1	210	210	212	201
	2	208	212	212	205
	3	208	212	212	205
	4	197	205	208	203
	5	165	195	199	163
Avg (2,3, & 4)		204	209	211	204

(a) . Away from spacer spring contact area.

(b) . At spacer spring contact area.

MIDDLE INTERMEDIATE SPACER LOCATION

Figure 6-14 Sections Through Middle-Intermediate Spacer Locations of Zr-Cr and Zircaloy-2 Fuel Rods

were located in identical axial positions in the dummy rod. The only difference was that the A and B type specimens were located 180 degrees apart on the tantalum rod to which they were attached.

The lower weight gain results on the "A" type specimens suggest that these specimens saw a similar type exposure as the dummy rod cladding. Thus, the "A" type specimens were probably next to the holes drilled in the cladding and were exposed to relatively fresh reactor water. The "B" type specimens would then be exposed to relatively static

reactor water away from the holes in the dummy rod cladding.

Since the weight gain results on these specimens were erratic and inconsistent, no direct comparison could be made between the weight gains in these specimens and the weight gains calculated from the oxide thickness on the dummy rod cladding. It is felt that the unique environment inside of the dummy rods has caused the erratic corrosion rates (especially on the Zr-Cr alloy).

7. COMPARISON OF IN-PILE AND OUT-OF-PILE CORROSION RESULTS

The design of the irradiation experiment was such that the effects of heat transfer, irradiation, and surface pretreatment on the corrosion rates of the Zr-Cr alloy could be separated and directly compared with these effects on the corrosion rates of the Zircaloy-2 alloy. The weight gain results from the in-pile and out-of-pile corrosion tests are summarized in Table 7-1. Since the CL-1 corrosion loop operates at 545°F, 1000 psi, and Consumers Big Rock Point reactor operated at 580°F, 1325 psi, care should be taken in quantitatively comparing in-pile and out-of-pile corrosion rates.

Two important trends are evident from the data:

- a. Both the Zircaloy-2 and Zr-Cr alloys' in-pile isothermal specimens have higher weight gains than the out-of-pile isothermal specimens after approximately 7900 hours of exposure. Since the in-pile weight gains for the Zr-Cr alloy are less than the weight gains for the in-pile Zircaloy-2 specimens, it appears the Zr-Cr alloy may be less sensitive than the Zircaloy-2 alloy to irradiation-enhanced corrosion. The data does not indicate any sensitivity of the in-pile corrosion rates to initial surface pre-treatment of the specimens for either the Zircaloy-2 or the Zr-Cr alloy.
- b. After 7900 hours of exposure, the Zircaloy-2 and Zr-Cr specimens from the fuel rod specimens have lower

uniform corrosion rates than the isothermal in-pile specimens. It seems logical that one would expect the fuel rod cladding to corrode at least as much as the in-pile isothermal specimens, and more, since the scale deposits should result in higher cladding temperatures. However, the weight gains on the fuel rod cladding are consistently lower than their comparison in-pile isothermal specimens. The results indicate that the scale apparently is protective up to these exposures.

The data does not clearly establish the effect of surface pre-treatments on the corrosion rates of either the Zr-Cr alloy or the Zircaloy-2 alloy. There are some indications that the corrosion rate increases with increasing temperature of the surface pre-film autoclave treatment for both the Zr-Cr and the Zircaloy-2 alloys.

In general, the data suggests the Zr-Cr alloy has slightly better in-pile uniform corrosion resistance than the Zircaloy-2 alloy. The in-pile isothermal Zr-Cr specimens consistently had lower weight gains than the Zircaloy-2 isothermal specimens. Two of the Zr-Cr clad fuel rods had lower weight gains than their counterpart Zircaloy-2 clad fuel rods. The results are gratifying since the Zr-Cr alloy was developed for high-temperature applications and the alloy was not expected to perform any better than the Zircaloy-2 alloy at these lower temperatures.

8. SUMMARY

As a result of the original Specific Zirconium Alloy Design Program (PA-24), a Zr + 2.0 wt % Cr + 0.16 wt % Fe alloy, designated Zr-Cr alloy, was developed with the potential for improved service reliability as a boiling water reactor fuel cladding. This alloy was shown to have far better high temperature ($> 300^{\circ}\text{C}$) corrosion resistance than Zircaloy-2 and therefore potentially offers protection against over-

temperature conditions which could result in excessive corrosion for the present water reactor cladding alloys.

A commercially feasible fabrication process has been developed and successfully used to fabricate significant quantities of tubing and bar stock from large ingots of the Zr-Cr alloy. Characterization tests have demonstrated that

TABLE 7-1
SUMMARY OF CORROSION RESULTS ON IN-PILE AND OUT-OF-PILE
ZIRCALOY-2 AND Zr-Cr TEST SPECIMENS

Weight Gains Mg/dm²

Surface Pretreatment	Zircaloy-2			Zr-Cr			
	Isothermal Out-of-Pile (a)	Isothermal In-Pile (b)	Fuel Rods In-Pile	Isothermal Out-of-Pile (a)	Isothermal In-Pile	Heat Transfer Out-of-Pile (a)	Fuel Rods In-Pile
As-Etched	15.6	69	58	15.6	62	15.6	42
300° Preoxidation for 60 hours	—	76	39	—	64	—	48
400° Preoxidation for 14 hours	22.2 (c)	78	57 (126) (d)	18.2 (c)	56	20.3	53 (145) (d)

- (a) Results from CL-1 corrosion loop tests; preoxidation weight gain is included for the preoxidized specimens.
 (b) Dummy rod cladding.
 (c) Second set of specimens in CL-1 loop; data extrapolated to ~ 7900 hours.
 (d) Total average weight gain, including thick oxide patches.

the commercially fabricated tubing's high temperature (500°C) corrosion resistance was not as good as that for laboratory melts, but still far exceeds the corrosion resistance of Zircaloy-2 at the same high temperatures. The mechanical properties of the Zr-Cr tubing closely resemble those of Zircaloy-2. The slight differences between the mechanical properties of the two alloys have not been fully explored; however, the alloy properties appear to be fully adequate for fuel cladding applications.

The advantage of the excellent high temperature corrosion resistance is offset in part by the slight decrease in creep strength and higher macroscopic neutron cross section.

The Zr-Cr alloy has a macroscopic neutron cross section slightly higher than the macroscopic neutron cross section of Zircaloy-2. The calculated macroscopic cross section for the Zr-Cr alloy is 0.0105, compared with 0.0084 to 0.0091 for other Zircaloy-2 composition range (the stainless steel value is 0.2600).

In addition, since the homologous temperature for the Zr-Cr alloy is lower than homologous temperature for Zircaloy-2, it is expected that the creep strength of the Zr-Cr alloy is slightly lower than the creep strength of Zircaloy-2. Although no creep data have been obtained, the lower stress rupture values for the Zr-Cr alloy tend to confirm the conclusion that the alloy may have a lower creep strength.

To obtain tubing with the superior corrosion resistance, particular attention must be paid to the fabrication process. Section 3 contains a detailed, step-by-step, fabrication schedule to produce Zr-Cr tubing with adequate physical and mechanical properties. The process closely resembles the fabrication schedule for Zircaloy-2 tubing, and any additional costs should be nominal. There are some specific process controls required to ensure that some Cr is in solid solution before the cold reductions and annealing; that is, the complete homogenization of the forged material must be accomplished before extrusion to tube shells. The normal practice of post-extrusion annealing before cold reduction has been eliminated. Section 2 provides the necessary background for the physical metallurgy of the alloy and explains the need for particular unique steps in the fabrication schedule.

The corrosion behavior of the Zr-Cr alloy like that for all zirconium alloys, is significantly affected by the N₂ content of the alloy. A thorough study was completed to establish the effect of N₂ content on the corrosion rate of the alloy, and the results are presented in Appendix C. As a

practical limit, the maximum N₂ content recommended in the alloy is 60 ppm.

The Zr-Cr alloy does require a slightly different procedure in surface preparation than does Zircaloy-2. To remove residual fluoride ions left in thin-surface films that developed during the normal zirconium etching processes, a new process was adopted and is given in Appendix B.

The Zr-Cr clad fuel rods have been successfully irradiated in Consumers Big Rock Point reactor since June 1967, and have accumulated an average exposure of ~ 14,300 MWd/TU. The Zr-Cr clad rods have performed as well as—and better than, according to some indications—Zircaloy-2 clad rods under similar irradiation conditions.

A detailed post-irradiation examination to evaluate the corrosion behavior of the Zr-Cr alloy as a fuel cladding has been performed on nine fuel rods (six Zr-Cr clad rods and three Zr-2 clad rods) irradiated to an average exposure of 8000 MWd/TU (7900 hours), and two nonfueled dummy rods also exposed for 7900 hours. For these exposures, the Zr-Cr alloy has performed satisfactorily as a fuel rod cladding. Oxide film thickness measurements of the fuel cladding indicate the Zr-Cr alloy's corrosion behavior in-pile is as good as or better than the corrosion behavior of Zr-2.

Long term, out-of-pile, loop corrosion tests have been performed on the Zr-Cr alloy and Zircaloy-2. The corrosion loop simulates the environments (including heat transfer) fuel rods would be exposed to in a boiling water reactor. The results of these corrosion tests after a 7800-hour exposure have been compared directly with the in-pile corrosion results, and the effects of heat transfer, irradiation, and surface pretreatment on the corrosion rates of the Zr-Cr alloy have been evaluated. Up to 7800 hours exposure, heat transfer conditions have no effect on the in-pile or out-of-pile corrosion rate of the Zr-Cr alloy. Irradiation conditions enhance the corrosion rate of both the Zr-Cr and Zr-2 alloy. The in-reactor weight gains measured were about three to four times those measured after out-of-pile corrosion. The effect of surface pretreatment on the in-pile corrosion rates of the Zr-Cr and Zr-2 alloys is not clear. However, there are some indications that the corrosion rates increase slightly with higher temperature autoclave prefilms.

The Zr-Cr alloy has shown some sensitivity to specific and unique corrosion environments, both in-pile and out-of-pile. In the CL-1 loop, the Zr-Cr alloy showed relatively high corrosion rates in the saturated steam environment. This behavior is contrary to results in steam autoclave tests.

REFERENCES

1. Klepfer, H. H., "Specific Zirconium Alloy Design Program Summary Report," April 1964 (GEAP-4504).
2. Patent No. 3,287,111, "Zirconium Base Nuclear Reactor Alloy," issued November 22, 1966.
3. ASTM B353, "Wrought Zirconium Alloy Seamless and Welded Tubes for Nuclear Service."
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7. Ibrahim, E. F., "An Equation for Creep of Cold Worked Zircaloy Pressure Tube Material," AECL-2528 (December 1965).
8. Anderson, W. K., et al., "Reactor Structural Materials: Engineering Properties as Affected by Nuclear Reactor Service," ASTM Spec. Tech. Pub. 314 (1962).
9. Johnston, A. B., Jr., "In-Reactor Oxidation of Zirconium Alloys in pH 10 Li OH and pH 10 NH₄ OH." BNWL-SA-822 (January 24, 1967).

APPENDIX A. REPORTS ISSUED

Presented in this appendix is a list of all of the reports issued since the inception of the Specific Zirconium Alloy Design Program in 1964.

Klepfer, H. H., "Specific Zirconium Alloy Design Program Summary Report," April 1964 (GEAP-4504)

Klepfer, H. H., et al., "Specific Zirconium Alloy Design Program, Quarterly Progress Report No. 8," April 1965 (GEAP-4821)

Klepfer, H. H., et al., "Specific Zirconium Alloy Design Program, Quarterly Progress Report No. 9," July 1965 (GEAP-4840)

Klepfer, H. H., et al., "Specific Zirconium Alloy Design Program, Quarterly Progress Report No. 10," October 1965 (GEAP-4960)

Klepfer, H. H., et al., "Specific Zirconium Alloy Design Program, Quarterly Progress Report No. 11," January 1966 (GEAP-5065)

Klepfer, H. H., and Blood, R. E., "Specific Zirconium Alloy Design Program, Quarterly Progress Report No. 12," April 1966 (GEAP-5134)

Klepfer, H. H., et al., "Specific Zirconium Alloy Design Program, Quarterly Progress Report No. 13," July 1966 (GEAP-5188)

Klepfer, H. H., "Specific Zirconium Alloy Design Program, Quarterly Progress Report No. 14," Memo, October 1966

Klepfer, H. H., et al., "Specific Zirconium Alloy Design Program, Quarterly Report Nos. 15 and 16," April 1967 (GEAP 5424)

Klepfer, H. H., et al., "Specific Zirconium Alloy Design Program, Quarterly Progress Report No. 17," July 1967 (GEAP-5516)

Duncan, R. N., et al., "Specific Zirconium Alloy Design Program, Quarterly Progress Report Nos. 18 and 19," January 1968 (GEAP-5603)

Duncan, R. N., et al., "Specific Zirconium Alloy Design Program, Quarterly Progress Report Nos. 20 and 21," July 1968 (GEAP-5649)

Busboom, H. J., et al., "The Fabrication and Characterization of Zr-Cr Alloy Tubing," February 1968 (GEAP-5589)

Mehner, A. S., et al., "Specific Zirconium Alloy Design Program, Quarterly Progress Report Nos. 22 and 23," January 1969 (GEAP-5743)

Mehner, A. S., and Klepfer, H. H., "Specific Zirconium Alloy Design Program, Quarterly Progress Report No. 24," April 1969 (GEAP-10026)

APPENDIX B. ETCHING AND CLEANING PROCEDURE FOR THE Zr-Cr ALLOY

The Zr-Cr alloy does require a slightly different procedure in sample preparation for corrosion exposure than Zircaloy-2. During vendor pickling, it was noticed that nominal Zr-2 pickling solutions (3 to 4% HF + 40% HNO₃ + 56-57% H₂O) leave Zr-Cr with a faint, dark-colored, thin-surface film; this was also observed when preparing corrosion specimens. Flouride ions detrimental to corrosion performance were found associated with these films — even after rinsing: 90 to 125 $\mu\text{gF}/\text{dm}^2$ versus 10 to 30 $\mu\text{gF}/\text{dm}^2$ normal analytical blank (a value consistent with that reported by two other investigators).^{*} It is necessary to keep the HNO₃ concentration above 45% to avoid formation of the faint, dark film during pickling or etching Zr + Cr + Fe alloys. For further assurance, it is necessary to use some positive mechanical means of removing residual surface contaminants during the rinsing operation (which

must follow immediately after etching). Analysis by pyrohydrolysis of etched samples showed that either ultrasonic cleaning or nylon brushing in the rinse brought the residual surface flouride down to the level of the analytical blank.

For laboratory studies, the following procedure was adopted and is strongly recommended:

- a. Etch in 50% HNO₃ + 3.5% HF + 46.5% H₂O to remove 0.0025 cm from each surface,
- b. Immediately rinse and brush with a nylon brush under flowing distilled water, and
- c. Dry on a paper towel.

^{*} See GEAP-4821, "Specific Zirconium Alloy Design Program Quarterly Report No. 8," April 1965, p. 37.

APPENDIX C. TOLERANCE OF THE Zr-Cr ALLOY FOR NITROGEN CONTAMINATION

The variable corrosion behavior of the first vendor batch of tubing made of the alloy raised the possibility (later discounted) that the tubing was contaminated with nitrogen. Knowledge of the quantitative effect of nitrogen on corrosion behavior would clearly be useful, in any event, in evaluating the alloy for practical application. The composition was suspect since tin is believed to mitigate the adverse effect of nitrogen on zirconium alloy corrosion, and tin was purposely excluded in the Zr-Cr composition; tin increases the corrosion rates of zirconium alloys, particularly at higher temperatures ($> 300^{\circ}\text{C}$).

Air is the source of nitrogen contamination of concern; in normal fabrication time periods, very high temperatures ($> 900^{\circ}\text{C}$) are required for significant contamination below the immediate surface accessible to simple and normal etching procedures. When the alloy is molten, it is most vulnerable to contamination of practical importance. Over 10 years of large-scale industrial melting of zirconium alloys with resulting nitrogen levels of 20 to 40 ppm against specifications of 60 to 80 ppm relieves much of the concern about the practical importance of nitrogen pickup during melting. At General Electric, hundreds of thousands of automatic welds of Zircaloy-2 end caps to fuel rods have been made without detectable nitrogen contamination (or performance consequence). Therefore, unless the Zr-Cr alloy were extremely sensitive to nitrogen contamination at levels below the Zircaloy-2 specification levels for nitrogen, there is little evidence that the nitrogen contamination could be a serious practical problem.

To determine whether the alloy was extremely sensitive to nitrogen contamination at levels of practical interest, coupons of Zr + 2.0 at.% Cr + 0.16 at.% Fe containing various nitrogen contents to 200 ppm were specially prepared and exposed for 2500 hours at 300, 400, and 500°C in high-pressure, refreshed steam (25 ppm O_2 and 3 ppm H_2). Difficulty was first encountered in preparing melts with uniform nitrogen distribution*; the successful procedure and the results are summarized in the following text.

C.1 INGOT PREPARATION

A high-purity zirconium bar stock electrode was double-arc-melted, with alloying elements added in the form of 0.025-cm iron wire and chromium electrolytic

flake. The analysis of the base ingot is given in Table C-1. Six 100-gram, flat segments were cut at random from the 1.8-kg ingot.

C.2 PREPARATION OF THE NITROGEN MASTER ALLOY

A nitrogen master alloy was melted by backfilling the melt chamber to 1/10 atmosphere of nitrogen gas and then melting a 50-gram Zr-Cr button with a nonconsumable

TABLE C-1
ANALYSIS OF THE NITROGEN EXPERIMENT INGOT

Alloy Analysis (wt%)

Element	
Cr	1.12 ± 0.04
Fe	0.095 ± 0.005

Impurity Analysis (ppm)

Al	20
B	< 0.2
C	< 80
Cd	< 0.2
Co	< 10
Cu	< 20
Hf	105
Mg	--
Mn	< 20
Mo	--
N	< 20
Ni	< 35
Na	--
Pb	< 20
Si	< 30
Sn	--
Ti	< 20
U	< 1
V	--
W	< 50
H	7

Average Hardness: 129 BHN

* See "Specific Zirconium Alloy Design Program" Quarterly Reports No.9 (GEAP-4840, July 1965) p. 19, No. 10 (GEAP-4960, October 1965) p. 37, and No. 11 (GEAP-5065, January 1966) p.6.

tungsten electrode. The button was melted six times on each side. Nitrogen analysis of the master alloy gave 35,550 ppm nitrogen. The master alloy was brittle and easily broken to provide small pieces to be inserted in precalculated amounts into holes drilled into both sides of the 100-gram ingot sections.

Each section containing the appropriate amount of master alloy was nonconsumably arc-melted (argon atmosphere) six times on each side. The resulting 100-gram buttons were forged at 955°C, solution treated for 1 hour at 955°C, quenched into water, and hot-rolled at 605°C. Hot-rolled sheet was sectioned (approximately 0.5-cm squares) and remelted to ensure complete homogenous distribution of the nitrogen.

C.3 FABRICATION OF SHEET

The six multiple-melted, 100-gram buttons were again fabricated, this time to 0.127-cm sheet, by this schedule:

Forge	955°C
Solution	955°C - 1 hour
Quench	30 seconds - water
Hot roll	605°C
Cold roll	40%

After each heating, twice the calculated air (nitrogen) contamination diffusion depth was removed by etching the surface.

C.4 CORROSION COUPONS

Fifteen corrosion coupons, 1.1 cm by about 4 cm, were sectioned from each of the six cold-worked sheets; the coupons were annealed in vacuum 2 hours at 760°C and air cooled. Each coupon was prepared for corrosion test by the procedure given in Appendix B. Each of the six sheets was sampled at two or more places, and analyzed several times for nitrogen content. Table C-2 lists the results of these nitrogen analyses.

C.5 RESULTS

Coupons were weighed after exposure for 168, 456, 1500, and 2500 hours at each of three temperatures (300, 400, and 500°C) in 1000-psi, refreshed, oxygenated (25 ppm O₂ + 3 ppm H₂) steam. Statistical analysis of the data gave the dependence of the steady-state corrosion rate (CR =

mg/dm²/day) on nitrogen content (N) and reciprocal absolute temperature (1/K) as

$$\ln CR = 10.8 + 0.005 N - 85 (1/K),$$

where the 95% limits on the constant coefficients are:

$$\begin{aligned} 10.8 \pm 0.7, \\ 0.005 \pm 0.004, \text{ and} \\ 85 \pm 4. \end{aligned}$$

The experimental data have been compared to this relationship in Figure C-1.

TABLE C-2
NITROGEN ANALYSES

Nominal Level (ppm N ₂)	Analyzed Level (ppm N ₂)
20	1 - 52, 51
50	1 - 76, 73
	2 - 73
	3 - 77
	4 - 75, 77, 74
75	1 - 86, 89
100	1 - 107, 108
	2 - 110
	3 - 112
	4 - 104, 104
150	1 - 154, 154
200	1 - 189, 189
	2 - 199, 202
	3 - 188
	4 - 188

C.6 DISCUSSION

For perspective, the corrosion rate of Zr-Cr alloy with 200 ppm N₂ (2.5 times the commercial specification for zirconium alloys) was still two to five times lower at all test temperatures than that for specification Zircaloy-2. Even at 500°C, with 200 ppm nitrogen for exposures to 2500 hours, the Zr-Cr alloy showed no transition or "breakaway" in the corrosion curve. (Such transitions are typical for specification Zircaloy-2 and -4 in less than 1/5 this time at 400°C and above.)

Figure C-1 Corrosion Rate Data Compared to Model Predictions.

French investigators** have studied the Zr-Cr alloy contaminated with even higher (200 to 995 ppm) nitrogen levels and concluded that it is necessary to add 0.5 wt % Sn to the alloy to give the required low sensitivity to these very high nitrogen levels. It is clear, however, for reasons

discussed previously, that contamination levels above 200 ppm are not typical of careful fabrication practice for zirconium alloys and fuel elements. The tin addition negates the Zr-Cr alloy design objective of improved high-temperature steam corrosion resistance.

** J. Delafosse and P. Poeydomenge, "Etude de l'influence de l'azote sur les alliages du type zirconium-chrome-fer," International Conference on the Use of Zirconium Alloys in Nuclear Reactors, "Zirconium '68," Marianske Lazne, Czechoslovakia, 1-3 October 1968.

APPENDIX D. CORROSION TEST FACILITIES

A special, high-pressure, low-flow, refreshed-steam corrosion system consisting of three 145-liter stainless steel autoclaves and associated equipment was developed* for corrosion tests at 300, 400, and 500°C. The important corrosion system parameters were:

- a. *Pressure.* A constant specific steam volume of 48.7 cc/gm, which is equivalent to pressures of 46 atm at 300°C, 58 atm at 400°C, and 68 atm at 500°C, was chosen.
- b. *Flow Rate.* A steam flow of 3 cm/sec was maintained in the sample section.
- c. *Oxygen and Hydrogen.* Controlled additions of 25 ± 7 ppm O_2 and 3 ± 2 ppm hydrogen were made to simulate radiolytic decomposition of steam.

d. *Water.* Deionized water of 1 megohm resistance was heated to provide the test steam.

e. *Temperature.* Temperature variations across the sample section were measured to be less than 2°C and control was $\pm 5^\circ C$.

Steps were taken to ensure that departures from a homogeneous environment would not affect the alloy comparisons. The autoclave was divided into 16 regions, within each of which one coupon of each alloy was tested. In addition, the coupon placement within each region was deliberately made random. (Evidence for a minor lack of homogeneous autoclave environment was, in fact, detected in the test data; the precautions taken permitted the effect to be removed in data analysis without bias in the alloy comparisons.)

* Nelson, W. B., "A Controlled-Environment Steam Corrosion Facility," GEAP-4393 (1963).

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